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LXI. *The Low Voltage Arc in Cæsium Vapour.* By

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[Plate VIII.]

1. *Introduction.*

IN previous papers † it has been shown that the normal operation of an arc in sodium and potassium vapours results in the excitation of a line-by-line spectrum corresponding to changes of orbit involving less energy than the ionizing potential. The present work describes similar experiments that have been made with cæsium vapour.

Foote and Meggers ‡, using a two-electrode discharge tube, photographed the cæsium spectrum at various accelerating voltages from λ 3878 to λ 9208 on dicyanin-stained plates. They found no evidence of group or single series spectra, but they proved the existence of a single-line spectrum—λ 8521, λ 8943. This doublet was produced alone under excitation of 1·5 to 3·9 volts accelerating field, and the intensity of both of these lines gradually increased at a rate proportional to the total number of electrons reaching the anode until the ionization potential was reached ; at this point there was a marked decrease in intensity of the lines. This decrease occurred at that voltage at which the complete

* Communicated by the Author.

† Phil. Mag. l. p. 165 (1925) and l. p. 796 (1925).

‡ Phil. Mag. xl. p. 80 (1920).

spectrum was produced and can be explained on the basis of Bohr's theory of atomic structure. The lines of the doublet $1\sigma - 1\pi_{12}$ result from inelastic collisions with electrons possessing energy between 1·38 and 3·9 volts, but as the latter voltage is exceeded electrons which at a slightly lower voltage give rise to the lines $1\sigma - 1\pi_{12}$ now produce the complete series spectrum, and any line of the series $1\sigma - m\pi$ is necessarily excited at the sacrifice of $1\sigma - 1_{12}$. These experimenters found that at voltages between 3·9, the ionizing potential, and 2·7, corresponding to $1\sigma - 2\pi$, there was an emission of $1\sigma - 2\pi$, *i. e.*, λ 4593, λ 4555, which could, however, be attributed to ionization. The electrons emitted by a heated cathode have a velocity distribution given by Maxwell's law, and even at a dull red heat a fraction of the electrons have a velocity 0·5 volt greater than the applied potential, so that the excitation of lines, other than λ 8943, λ 8521, below the ionization potential is explained by the small number of high velocity electrons present. So it was concluded that only two types of inelastic collision occur between electrons and atoms of cæsium vapour, viz., at the resonance and ionizing potentials respectively.

In view of this conflict between theory and experimental results, Hughes and Hagenow* repeated the experiment with an apparatus which was essentially a three-electrode discharge tube having a nickel plate and grid. The cæsium, obtained by heating a mixture of cæsium chloride and cæsium turnings, condensed on the surface of the nickel cathode and formed a very convenient thermionic source, yielding a copious supply of electrons below dull red heat. They found that the blue doublet, λ 4555, λ 4593, appeared with accelerating voltages between 2·8 and 3·0 volts, and the spectrograms showed satisfactory evidence of a step-by-step excitation, especially in the principal series; the results for the two subordinate series were not definite. No line in the latter series apppeared at 3·5 volts, although they were all excited at 3·7–3·8 volts except λ 6983, λ 6973, for which the plate was probably insensitive.

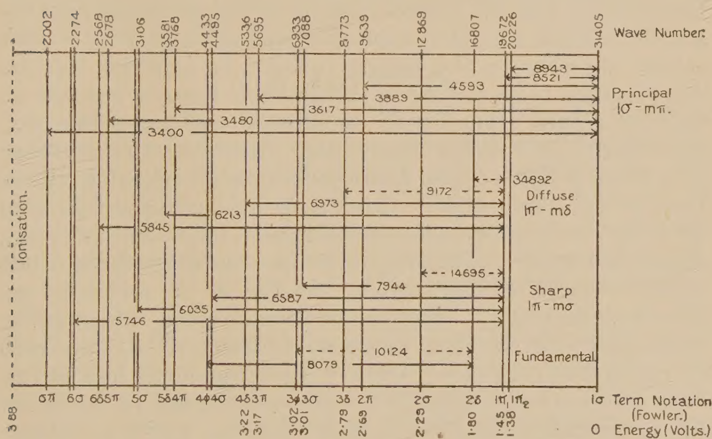
Theory indicates that the valence electron within the atom can be displaced from the normal orbit, 1σ, directly to any $m\pi$ orbit as a result of inelastic collision with the proper energy exchange, and as the probability of transfer from an $m\pi$ orbit to the 1σ orbit decreases rapidly as m increases, the probability of the displacement of the electron to an $m\pi$ orbit as the result of electron-atomic collisions decreases as

* Phys. Rev. xxiv. p. 229 (1924).

m increases, even though all of the impacting electrons have energy corresponding to $1\sigma - m\pi$.

Considering the schematic representation of the cæsium atom shown in fig. 1, falls from the $m\pi$ orbits to the normal orbit, 1σ, give the principal series consisting of pairs with diminishing separation. Transfers from the σ and δ rings to the two adjacent orbits, represented by $1\pi_1$ and $1\pi_2$, yield the constant separation pairs of the sharp and diffuse series respectively; falls from the $m\phi$ orbits to the orbit 2δ give the fundamental series consisting of single lines. The horizontal lines extending between orbits indicate the wave-length of the radiation emitted by energy falls between the

Fig. 1.



Graphical representation of caesium atom.

orbits, the wave-lengths falling outside the range of sensitiveness of the photographic plate being indicated by dotted lines. Since the selection principle allows only those transfers in which the azimuthal quantum number changes by unity, and as these numbers for the $m\sigma$, $m\pi$, $m\delta$ and $m\phi$ orbits are respectively 1, 2, 3 and 4, interorbital transfers from the $m\pi$ to the $m\sigma$ or the $m\delta$ orbits are permitted.

The energy level of the various orbits has been expressed also in terms of the potential difference through which the bombarding electron must fall in order to accumulate kinetic energy equivalent to a quantum of radiation of wave number ν. To the innermost orbit zero energy is ascribed, and the requisite energy which the bombarding electron

must possess to displace the valency electron to any orbit is denoted against that orbit. For example, 1·38 volts, indicated at the $1\pi_2$ orbit, represents the impacting energy necessary to displace the electron from the 1σ to the $1\pi_2$ orbit, and radiation of λ 8943 is emitted when the electron returns from the temporary to the stable orbit. Theoretically it should be possible to excite λ 8943 without λ 8521, providing that the impacting energy lies within the range 1·38–1·45 volts, but in actual practice it would be difficult, if not impossible, to insure that no electrons in such a stream exceeded the higher limit of this energy range because of the distribution of velocities among the electrons emitted from an incandescent cathode. Colliding electrons of 2·69 volts energy should displace the valency electron to the 2π orbit, and the second doublet of the principal series—λ 4593, λ 4555, should be excited when the displaced electrons return directly to the normal orbit. In addition to the direct return from the 2π to the 1σ orbit there is possible an indirect return from the 2π to the $1\pi_1$ and $1\pi_2$ orbits, and from there to 1σ, the latter step involving the emission of λ 8943, λ 8521. The Bohr principle of selection shows that in the absence of a disturbing field a direct fall from 2π to $1\pi_1$ or $1\pi_2$, with the emission of $2\pi-1\pi_1$, $2\pi-1\pi_2$, should not occur. The transition between these three orbits must be made through either the 2σ or 2δ orbit as an intermediate stage. The lines excited at these intermediate stages, $2\sigma-2\pi$, $2\delta-2\pi$, would not be observed, as they both lie far in the infra red. When cæsium vapour is bombarded with electrons of energy 2·69 volts—corresponding to the 2π orbit—radiation of λ 8943, λ 8521; λ 4593, λ 4555; λ 34892, λ 30100; λ 14695, λ 13588 should be excited by interorbital transfers permitted by the selection principle, in addition to the lines $2\sigma-2\pi$ and $2\delta-2\pi$.

It should be noted that the valency electron returning to 1σ from $1\pi_1$ and $1\pi_2$ and giving rise to λ 8943, λ 8521, this radiation may be absorbed by any neighbouring cæsium atoms, resulting in the ejection of the valency electron within these atoms to the $1\pi_1$ and $1\pi_2$ orbits. The excited or abnormal atoms thus formed may then be subjected to impacting energy of 2·69 volts, with the result that complete ionization is effected. Such a phenomenon is not likely to occur at low vapour pressures.

At present there is no evidence that the electron within the atom can be displaced to the $m\delta$ or $m\sigma$ orbits only by way of $1\pi_1$ and $1\pi_2$. Klein and Rosseland * have

* *Zeit. f. Physik*, iv. 1, p. 46 (1921).

suggested that a slow-moving electron in collision with an excited atom may gain kinetic energy while the atom is assuming its normal state, no radiation being emitted in the process, so that collisions can occur between free electrons and atoms in which the the atom bombarded passes without emitting radiation from a stationary state of greater energy into a stationary state of smaller energy, while the impacting electron acquires an amount of kinetic energy equal to the energy lost by the atom. This is the converse of excitation by collision. Franck * has extended this idea to collisions between excited and unexcited atoms, and explains the appearance of the mercury line $\lambda\,2537 - 1S - 1p_2$, when mercury vapour is excited by $\lambda\,1849 - 1S - 1P$, by supposing a transition occurs without radiation from the 1P orbit to the $1p_2$ state.

2. *Experiments.*

A three-electrode discharge tube was used; the electrons emitted from a heated tungsten wire cathode were accelerated by a potential difference applied between the grid and the cathode, and entered a force-free space bounded by the grid and anode. Light from the immediate neighbourhood of the grid was focussed on the quartz spectrograph, and the spectra at various exciting potentials were photograped on dicyanin-stained plates. The whole of the discharge bulb, containing a small quantity of cæsium metal which had been distilled into the bulb from a side tube, was enclosed in an electric heater maintained at 120° C., the vapour pressure of cæsium at this temperature being less than 0·01 mm. of mercury. The residual gas pressure was maintained below 0·001 mm. of mercury by means of an oil pump running continuously.

The electron currents were of the order of 2 milliamperes, and the discrepancy between the applied voltages and the potential actually used inside the discharge tube was determined, and allowed for, by measuring the ionization potential and comparing the value so obtained with the theoretical result, 3·88 volts.

As the accelerating voltage was raised from zero no visible radiation appeared until at 2·7 volts a blue glow appeared in close proximity to the grid and plate. This blue glow represents the excitation of the second doublet of the principal series, $\lambda\,4593$, $\lambda\,4555$. Increasing the voltage still further, no change in the colour of the discharge

* *Zeit. f. Physik*, ix. 5, p. 259 (1922).

was observed until at 3·9 volts the whole of the space between the grid and the plate was filled with a violet coloured radiation. From these results it is evident that the space charge lowers the effective potential except in the immediate neighbourhood of the grid and anode.

The spectrograms obtained at different voltages are shown in Plate VIII. In the first spectrogram the doublet λ 8943, λ 8521 appears at 1·6 volts, and is followed at 2·7 volts by λ 4593, λ 4555 as shown in the second spectrogram. The next lines to be excited should be λ 9172, λ 8761 ; λ 7944, λ 7609 ; λ 3889, λ 3876, respectively, but no additional lines appeared on the plate until the potential difference was raised to 3·2 volts, at which accelerating voltage λ 7944, λ 7609 and λ 3889, λ 3876 were photographed—Spectrogram III. It is probable that λ 7944, λ 7609 were excited below 3·2 volts, but the intensity of the radiation was so feeble that these lines were not registered on the plate, even though exposures of several hours duration were made. No additional lines were photographed until the ionization potential—3·9 volts—was reached, when the entire arc spectrum of cæsium, as shown in the fourth spectrogram, was excited.

The various spectrum lines which appeared at different accelerating voltages are given in the following Table.

Series.	Wave-length.	Excitation voltage.	
		Experimental.	Calculated.
$\{1\sigma-1\pi_2$	λ 8943	1·6 volts.	1·38 volts.
$\{1\sigma-1\pi_1$	λ 8521	1·6	1·45
$1\pi_1\ \ 2\delta$	λ 34892	—	1·80
$1\pi_1-2\sigma$	λ 14695	—	2·29
$1\sigma-2\pi$	λ 4593	2·7	2·69
$1\pi_1-3\delta$	λ 9172	—	2·79
$1\pi_1-3\sigma$	λ 7944	3·2	3·01
$2\delta-3\phi$	λ 10124	—	3·02
$1\sigma-3\pi$	λ 3889	3·2	3·17
Complete arc spectrum		3·9	3·88

Although it was not possible to differentiate between the excitation of lines within the range 3·2–3·9 volts, probably

because the number of collisions resulting in excitation is small at the actual critical voltage, yet the evidence is in favour of a line-by-line excitation similar to that found with the other alkali metals.

The cost of the apparatus used in these experiments was defrayed by a Government grant, through the Royal Society, for which the author wishes to express his sincere thanks.

LXII. *The Separation of the Modified and Unmodified Scattering Coefficients of X-Rays.*

By G. E. M. JAUNCEY, *D.Sc., Associate Professor of Physics, and* O. K. DE FOE, *M.Sc., Washington University, St. Louis, U.S.A.* *

1. *Introduction.*

THE Compton effect(1) necessitates a new experimental procedure when the scattering coefficient of X-rays in matter is measured. In fact, on account of the modified and unmodified X-rays produced by the scattering process, it becomes necessary to recognize two scattering coefficients—one for the modified and the other for the unmodified X-rays. What has previously been called the linear scattering coefficient σ is more correctly the sum of σ_1, the unmodified linear scattering coefficient, and σ_2, the modified linear scattering coefficient. In all previous experiments the calculation of σ has been based on the assumption that when homogeneous X-rays are scattered, the scattered X-rays have the same absorption coefficient as the primary rays in the scattering substance. The result of this assumption is that the calculated values of σ, or more correctly of $\sigma_1+\sigma_2$, are all too small. However, due to the small change of absorption coefficient in the modified rays, the previously calculated values of σ are not far wrong.

Let us now distinguish between σ the spherical scattering coefficient, and s the linear scattering coefficient per unit solid angle in a direction ϕ with the forward direction of the primary rays. For polarized rays s is a function of both ϕ and of the angle between the electric vector of the primary rays and the plane of scattering. For our present purposes, however, we shall assume that the X-rays are

* Communicated by the Authors.

unpolarized, so that s is a function of ϕ only. In the experiments on scattering it is s which is first calculated from the experimental readings, and then σ is obtained from s by means of the formula

$$\sigma=\int_0^\pi 2\pi s \sin\phi \, d\phi. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In virtue of the Compton effect, s, like σ, consists of two parts—s_1, the linear scattering coefficient per unit solid angle in the direction ϕ for the unmodified rays, and s_2, a similar coefficient for the modified rays. The spherical coefficients σ_1 and σ_2 are related to s_1 and s_2 respectively by the formulæ

$$\sigma_1=\int_0^\pi 2\pi s_1 \sin\phi \, d\phi, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\sigma_2=\int_0^\pi 2\pi s_2 \sin\phi \, d\phi. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

2. *Theoretical Considerations.*

On Thomson's theory of scattering(2) s is given by

$$s=K(1+\cos^2\phi)/2, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$K=(NZ\rho/W)\,.\,(e^4/m^2c^4), \quad . \quad . \quad . \quad . \quad (5)$$

where N is Avogadro's number, Z the number of electrons per molecule of the scattering substance, ρ its density and W its molecular weight, e and m the charge and mass of the electron, and c the velocity of light *in vacuo*. For convenience let us represent the value of s as calculated from the experimental readings on the assumption that there is no change of absorption coefficient on scattering by s_{exp}. It is found that when moderately soft X-rays are scattered by light elements, s_{exp} is very nearly given by Eq. (4) for values of ϕ between about 50° and about 120°. However, even in this range s_{exp} shows a minimum at about 100° instead of at 90° as is required by the Thomson theory. For angles between about 15° and about 50° the phenomenon of scattering in excess of the Thomson amount, or excess scattering, is observed. For instance, a curve due to Barkla and Ayres(3) shows scattering of about twice the Thomson amount at 20°. The same effect has been observed by Hewlett(4), Jauncey and May(5), and others. At angles less than about 15° the scattering has been found by Hewlett, Jauncey and May, and others to fall quickly to zero. At

angles between about 120° and 180° s_{exp} is less than the Thomson value and we have reduced scattering. The predictions of the Thomson theory are therefore only in approximate agreement with experimental fact for the scattering of moderately soft X-rays by light elements in the range 50° to 120°.

In 1923, A. H. Compton (1) and P. Debye (6) proposed a quantum theory of scattering which demands a change of wave-length on scattering. In addition, the angular distribution of the intensity of the scattered rays was worked out by A. H. Compton (1) and Jauncey (7). The formula for s_2 as given by these writers is

$$s_2 = \frac{K\{1+\cos^2\phi + 2a_0(1+a_0)\operatorname{vers}^2\phi\}}{2(1+a_0 \operatorname{vers}\phi)^5}, \quad . \quad (6)$$

where $a_0 = h/mc\lambda_0$ and λ_0 is the wave-length of the primary rays. Eq. (6) is based on the assumption that the X-rays are scattered by free electrons originally at rest.

The values of s_2 for the range 50° to 180° agree more closely with s_{exp} than do the Thomson values of s. On the other hand, the theoretical values of s_2 do not agree at all with the excess scattering between 15° and 50° nor with the vanishing to zero of the scattering at angles less than 15°.

However, since the theoretical values of s_2 are derived from the assumption of free electrons at rest it is not surprising that at the small angles there is considerable departure from theory, as on the quantum theory it is at these small angles that the energy given to the scattering electron becomes small, and therefore the electron cannot be ejected from the atom at these small angles. As experimental evidence that some of the scattering electrons are not ejected, may be cited the fact of the existence of unmodified scattering as shown by the experiments of Compton (8) and Ross (9). On the theoretical side Jauncey has explained the existence of the unmodified scattering by taking into account the momentum and the binding energy of the scattering electrons. Jauncey's theory (10), (11) supposes that there is, for a given angle of scattering by a given type (K, L, etc.) of scattering electrons, a certain range of positions of the electron in its Bohr orbit from which the electron cannot be ejected by the scattering process, and that, in this case, the scattering takes place without change of wave-length. For positions outside of this range there is scattering with change of wave-length, although there is also a variation of this change of wave-length for a given

angle ϕ depending on the position of the scattering electron in its orbit [10], [11], [12]. In other words, Jauncey's theory of the unmodified line requires that, of the $NZ\rho/W$ electrons per unit volume of the scattering substance, there are at any instant of time $pNZ\rho/W$ electrons which are in such orbital positions that if one of these electrons scatters a quantum in the direction ϕ it will scatter with change of wave-length. If we consider the K electrons alone then the fraction p_K for the K electrons by Jauncey's theory is approximately given by

$$p_K = \frac{\alpha_0 \operatorname{vers} \phi + 2\sqrt{2\alpha_s} \sin \tfrac{1}{2}\phi - \lambda_0/\lambda_s}{4\sqrt{2\alpha_s} \sin \tfrac{1}{2}\phi}, \quad . \quad . \quad (7)$$

where $\alpha_s = h/mc\lambda_s$ and λ_s is the K critical absorption wave-length of the scattering substance. Similar formulæ hold for those L, M, etc. electrons which move in circular orbits, while more complicated formulæ exist for those electrons which are moving in elliptic orbits. Knowing the various fractions for the different kinds of electrons, it is an easy matter to obtain the average fraction for the whole atom. This we have denoted above by p, but since p is a function of ϕ we shall henceforth represent it by $p(\phi)$. The theoretical value of s_2, instead of being given by Eq. (6) is now given by

$$s_2 = \frac{Kp(\phi)\{1 + \cos^2\phi + 2\alpha_0(1+\alpha_0)\operatorname{vers}^2\phi\}}{2(1+\alpha_0 \operatorname{vers}\phi)^5}, \quad . \quad (8)$$

provided that the motion of the scattering electrons in their Bohr orbits has no effect on the angular distribution of the intensity of the modified scattered rays.

The value of $p(\phi)$ for the scattering of Mo Kα X-rays from carbon is approximately unity for angles greater than 75°, and hence s_{exp} should agree fairly well with the theoretical values of s_2 as given by Eq. (6), and this is found to be the case. However, for angles less than 45° the probability $p(\phi)$ becomes less than unity decreasing to zero at 5°, which is the region where excess scattering exists. Hence, if our theory is correct, this excess scattering is connected in some way with the theoretical prediction that at angles less than 45° a large part of the scattered rays is of the unmodified type. That this prediction is at least in qualitative agreement with fact is shown by the experiments of Ross [13], where he finds no modified line, or at least a modified line of very small intensity, relative to that of the unmodified line when Mo Kα X-rays are scattered at 30° by copper. Further support of the suggested connexion between excess scattering

and unmodified scattering is given by the fact that $s_{\exp}$ for copper is found by Barkla and White [14] to be greater than the Thomson value at 90°, and that the excess scattering becomes greater as the primary rays become softer. This is in accord with our theory, as $p(\phi)$ becomes less as the atomic weight of the scattering substance becomes greater and also as the wave-length becomes longer. Still further support of our idea is given by Compton's values for $s_{\exp}$ for the scattering of gamma rays. In Compton's paper [1] a curve is given showing how closely $s_{\exp}$ for gamma rays agrees with s_2, as given by Eq. (6), for the range 30° to 180°. For gamma rays $p(\phi)$ is very nearly unity at 30°, and hence the agreement.

In Jauncey's papers [10], [11] an expression is derived for the ratio of the energy of the modified to that of the unmodified rays scattered at a certain angle. The derivation, however, is based on the assumption that the energy scattered in a given direction ϕ is the same whether the scattering electron is scattering modified or unmodified rays. We do not feel, however, that this is necessarily so. In fact our experiments, so far, indicate that the energy in the unmodified rays is a greater fraction of the total energy in the modified and unmodified rays in a direction ϕ than is predicted by Jauncey's expression. It is our present idea that although the angular distribution of modified energy is given by Eq. (8), yet the angular distribution of unmodified energy is not necessarily given by replacing the factor $p(\phi)$ by the factor $\{1-p(\phi)\}$ in Eq. (8).

From the previous remarks in this section it is therefore obvious that it is very necessary to devise a method, or methods, of measuring both s_1 and s_2 experimentally in order to test our theory.

3. *Theory of the Experimental Methods.*

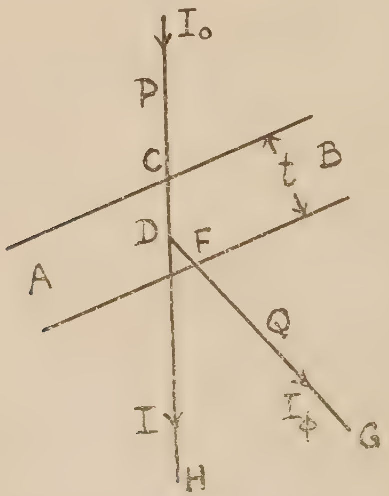
In both of the methods to be described a known thickness of absorbing material is transferred from a position where the primary X-rays pass through this material to a position where the scattered rays in a certain direction pass through the material before entering the ionization chamber. The first position we shall denote as the P position, and the second as the Q position. If all of the scattered rays in a certain direction ϕ are of the unmodified type, the intensity of the rays entering the ionization chamber will be unaltered by transferring the absorbing material from P to Q, provided that the intensity of the primary rays remains constant. However, if part of

the scattered rays are modified, part of the primary rays of wave-length λ_0 will be changed to rays of wave-length λ_ϕ, where λ_ϕ is given by the Compton equation [1]

$$\lambda_\phi - \lambda_0 = (h/mc) \operatorname{vers} \phi. \quad . \quad . \quad . \quad . \quad (9)$$

If we know λ_0 we can determine the absorption coefficient of the primary rays in the absorbing material by reference to a curve of absorption coefficients plotted against wave-length. Now making use of Eq. (9) we can, from the same curve, determine the absorption coefficient of the modified rays scattered in the direction ϕ in the absorbing material, or better still, the change of absorption coefficient on scattering. The intensity of the rays entering the ionization chamber when the absorbing material is at P is greater than when it is at Q, and the difference between the intensities when the absorbing material is at P and that when it is at Q is a function of the fraction of modified rays present in the scattered beam.

Fig. 1.



Method I.—This method is a modification of Crowther's method [15]. A beam of primary X-rays of intensity I_0 passes first through a thickness T_1 of absorbing material (in our experiments we use aluminium) placed at P and then falls upon a slab of scattering substance AB (fig. 1). The intensity of the primary rays arriving at D is therefore $I_0 e^{-(\mu_1 T_1 + \mu_3 x)}$, where μ_1 and μ_3 are the linear absorption coefficients of the primary rays of wave-length λ_0 (the primary rays are

supposed homogeneous) in the absorbing material and scattering substance respectively, and $x=\mathrm{CD}$. The intensity of the modified rays scattered by an element dx at D per unit solid angle in the direction ϕ is $s_2 \mathrm{I}_0 e^{-(\mu_1 \mathrm{T}_1+\mu_3 x)}\,dx$. These scattered rays traverse a distance DF in the scattering substance. The scattered rays then pass through a thickness R of air and a thickness T_2 of the absorbing material placed at Q and then enter the ionization chamber. If μ_2, μ_4 and μ_6 are the linear absorption coefficients of the modified scattered rays in the absorbing material, the scattering substance and air respectively, and A is the area of the ionization chamber window, the intensity of the modified rays entering the chamber is

$$(d\mathrm{I}_\phi)_{\mathrm{mod}}=\frac{\mathrm{A}s_2\mathrm{I}_0 e^{-(\mu_1\mathrm{T}_1+\mu_2\mathrm{T}_2+\mu_3 x+\mu_4 y+\mu_6\mathrm{R})}}{\mathrm{R}^2}dx, \quad . \quad (10)$$

where $y=\mathrm{DF}$, the distance R being great compared with T_2 and the thickness of the scattering slab. For the unmodified rays the intensity entering the ionization chamber window is

$$(d\mathrm{I}_\phi)_{\mathrm{unmod}}=\frac{\mathrm{A}s_1\mathrm{I}_0 e^{-(\mu_1\mathrm{T}_1+\mu_1\mathrm{T}_2+\mu_3 x+\mu_3 y+\mu_5\mathrm{R})}}{\mathrm{R}^2}\,.\,dx, \quad . \quad (11)$$

where μ_5 is the absorption coefficient of unmodified rays in air.

As in Crowther's method, the normal to a face of the scattering slab AB makes an angle $\phi/2$ with the direction of the primary rays. We then have $\mathrm{DF}=(t\sec\frac{1}{2}\phi-x)$, where t is the thickness of the scattering slab. The chamber is now swung around to H so as to receive the primary rays while the absorbing material which was at Q is now placed so that the primary rays pass through it. The intensity of the primary rays entering the chamber is I, where

$$\mathrm{I}=\mathrm{I}_0 e^{-(\mu_1\mathrm{T}_1+\mu_1\mathrm{T}_2+\mu_3 t\sec\theta+\mu_5\mathrm{R})}, \quad . \quad . \quad . \quad . \quad (12)$$

where $\theta=\phi/2$.

Eqs. (10) and (11) are added, obtaining $(d\mathrm{I}_\phi)_{\mathrm{total}}$. This last named quantity is then integrated from $x=0$ to $x=t\sec\theta$, and making use of Eq. (12) we obtain

$$\mathrm{I}_\phi=\mathrm{CI}\{s_1+s_2 e^{-(k\mathrm{T}_2+b)}(e^g-1)/g\}, \quad . \quad . \quad (13)$$

where
$$\left.\begin{aligned} \mathrm{C}&=\mathrm{A}t\sec\theta/\mathrm{R}^2\\ k&=(\mu_2-\mu_1)\\ b&=(\mu_6-\mu_5)\mathrm{R}+g\\ \text{and}\quad g&=(\mu_4-\mu_3)t\sec\theta \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13\,\mathrm{A})$$

In order to obtain s_1 and s_2 it is necessary to determine

the values of I_ϕ for two values of T_2, the thickness of the absorbing material in the scattered beam. However, in order to keep I constant it is necessary to keep (T_1+T_2) constant, even though T_2 is varied. This is accomplished by transferring a certain thickness d of the absorbing material from P to Q in fig. 1. Let i_1 and i_2 be the values of I_ϕ when T_2 has the values d_1 and d_2 respectively. We then find

$$s_2=\frac{g(i_1-i_2)}{\mathrm{CI}(e^g-1)e^{-(kd_1+b)}(1-e^{-kd})}, \quad . \quad . \quad . \quad (14)$$

and

$$s_1=\frac{i_2-i_1e^{-kd}}{\mathrm{CI}(1-e^{-kd})}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where $d=(d_2-d_1)$, the thickness of aluminium transferred from P to Q between the readings of i_1 and i_2. It is seen that the ratio of s_1 to s_2 can be obtained from Eqs. (14) and (15) provided that I, and therefore I_0, remains constant without a knowledge of I.

However, instead of measuring I_φ for two different values of T_2 when I (or I_0) is kept constant, we may keep $I\phi$ constant by varying I (or I_0).

Let I_1 be the value of I (or I_0) when T_2 has the value d_1 and I_2 the value of I when T_2 has the value d_2, then we obtain

$$\frac{s_2}{s_1}=\frac{g(I_2-I_1)}{(e^g-1)e^{-(kd_1+b)}\,.\,(I_1-I_2e^{-kd})}. \quad . \quad . \quad (16)$$

Method II.—In this method the slab of scattering material is set with the normal to a face of the slab bisecting the angle PDQ, as shown in fig. 2.

As in Method I. there is a thickness T_1 of absorbing material in the primary beam at P and a thickness T_2 of the same material at Q. In this case we suppose the slab to be so thick that no primary rays get through it as in Crowther's method, and we therefore integrate from $x=0$ to $x=\infty$ in obtaining I_ϕ. The formula of Eq. (13) is now replaced by

$$I_\phi=\mathrm{D}I_0\{s_1+\mathrm{B}s_2e^{-k\mathrm{T}_2}\}, \quad . \quad . \quad . \quad . \quad (17)$$

where

$$\left.\begin{aligned}\mathrm{D}&=\mathrm{A}/(2\mathrm{R}^2\mu_3)\\ \mathrm{B}&=e^{-h\mathrm{R}}/\{1+(\mu_4-\mu_3)/2\mu_3\}\\ h&=\mu_6-\mu_5\end{aligned}\right\} \quad . \quad . \quad (17\mathrm{A})$$

and

As in Method I. we may keep I_0 constant and measure the two values i_1 and i_2 of I_ϕ when we have the two values d_1 and d_2 of the thickness T_2; or we may keep I_ϕ constant and measure the two values I_1 and I_2 of I_0 when we have the

values d_1 and d_2 of the thickness T_2. In the former case (16)

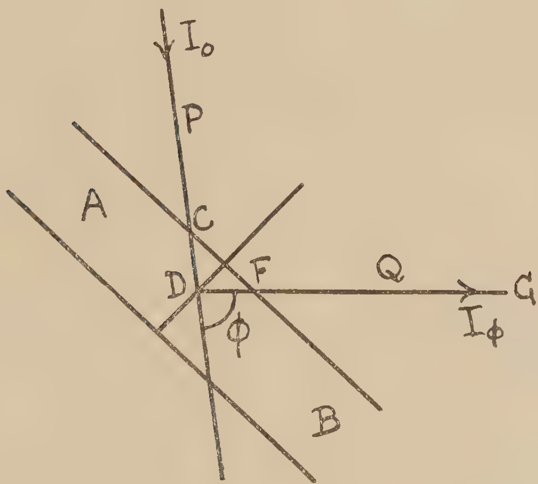
$$s_1 = \frac{i_2 - i_1 e^{-kd}}{DI_0(1-e^{-kd})}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and

$$s_2 = \frac{i_1 - i_2}{DBI_0 e^{-kd_1}(1-e^{-kd})}, \quad . \quad . \quad . \quad . \quad (19)$$

where $d=(d_2-d_1)$, the thickness transferred from P to Q.

Fig. 2.



In the latter case

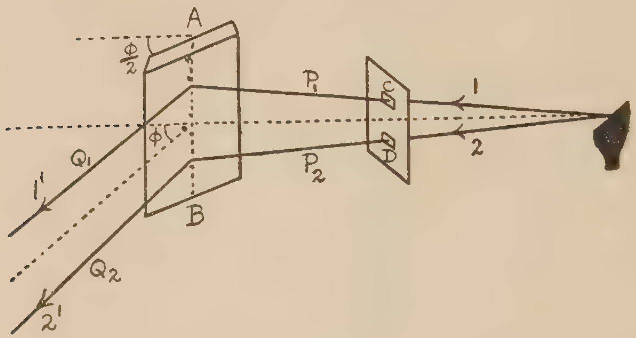
$$\frac{s_2}{s_1} = \frac{I_2 - I_1}{Be^{-kd_1}(I_1 - I_2 e^{-kd})}. \quad . \quad . \quad . \quad . \quad (20)$$

4. *Experimental Arrangement.*

Eqs. (16) and (20) suggest the use of a balance method for determining the ratio s_2/s_1. We have used Method II. and Eq. (20) for determining the ratio for copper as the scattering substance. Fig. 3 represents our experimental arrangement. Two primary beams 1 and 2, after passing through two slits C and D and thence through absorbing material placed at P_1 and P_2, fall upon the scattering block AB. From AB scattered beams $1'$ and $2'$ proceed through absorbing material at Q_1 and Q_2 and thence to two ionization

chambers. The inner electrodes of these two chambers are connected to the same electrometer, while the outer electrodes are connected to opposite potentials, so that if the intensities of the two scattered beams are the same the deflexion of the electrometer is zero. In our experiments the same thickness of aluminium is placed at P_1 as at P_2, while the thickness at Q_1 is the same as at Q_2. The opening of the slit at D is kept constant, while that of the slit at C is varied by means of a micrometer screw until the electrometer shows no deflexion and the reading of the micrometer recorded. A thickness d of aluminium is now transferred from P_1 to Q_1, no

Fig. 3.



aluminium, however, being transferred from P_2 to Q_2. The effect of this is that the intensity of beam 1′ entering the upper ionization chamber is less than that of beam 2′ entering the lower chamber. Hence, in order to bring back the balance it is necessary to open the slit at C and its micrometer reading is again observed. These two micrometer readings then replace I_1 and I_2 in Eq. (20). In order to find k in Eq. (20) it is necessary to know the wave-length of X-rays. This we have determined by placing sufficient additional aluminium at P_1 to double the width of the slit at C. From this added thickness we calculate the average wave-length of the primary rays.

To determine the absolute values of s_1 and s_2 we use Crowther's experimental method and calculate s_1 and s_2 from Eq. (13), since we already know the ratio s_2/s_1.

Our experimental results will be reserved for another paper, which we hope will appear in the near future.

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(1) A. H. Compton, Phys. Rev. xxi. p. 483 (1923).
(2) J. J. Thomson, 'Conduction of Electricity through Gases,' 2nd Ed., p. 325.
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(15) J. A. Crowther, Proc. Roy. Soc. lxxxvi. p. 478 (1912).
(16) A brief announcement of Eqs. (14), (15), (18) and (19) is given by De Foe and Jauncey in Proc. Nat. Acad. Sci. xi. p. 517 (1925).

Washington University.
St. Louis, Mo., U.S.A.
October 23, 1925.

LXIII. *Enhanced Lines produced by the Interrupted Arc in Sodium and Potassium Vapours.*

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[Plate IX.]

1. *Introduction.*

IT is well known that although the enhanced lines of various metals occur chiefly in the spark discharge, some appear in the arc burning between metallic electrodes, particularly at that part of the arc in the vicinity of the poles †. The emission of enhanced lines under these conditions has been attributed to the high potential gradient at the electrodes, which results in the electrons at these regions attaining impacting energy sufficient to eject the second electron from the atom. It has been found by Crew ‡, and by Fowler and Payne §, that the spark lines in the arc become prominent in the presence of hydrogen,

* Communicated by the Author.
† Duffield, Astrophys. Jour. xxvii. p. 260 (1908). Fabry and Buisson, *Jour. d. Phys.* ix. p. 929 (1910).
‡ Astrophys. Jour. xii. p. 167 (1900).
§ Proc. Roy. Soc. A, lxxii. p. 253 (1903).

although in general this gas does not seem to be essential for the excitation of such lines.

An exhaustive study of the occurrence of these lines in the arc discharge has been made by Hemsalech and de Gramont *, who used an arc passing between a metal, placed on a copper plate, and a pointed carbon rod which, fixed vertically above the metal, could be raised or lowered as desired. They found that the spark lines flashed into prominence in the arc discharge as the degree of ionization was lowered, which was brought about, for example, by blowing air across the arc. The lines disappeared when the carbon rod, acting as the cathode, became white hot, but were intensified by cooling the electrodes to $-190°$ C. by immersion in liquid air. They also attained a high degree of development if a drop of liquid which offered a comparatively high resistance was placed between the poles before starting the arc. This excitation of the enhanced lines in this liquid film arc was independent of the nature of the liquid, provided that the distance between the electrodes did not exceed 0·1–0·5 mm. At greater distances the liquid film was destroyed, and a second phase of the arc followed in which a transitory flash passed between the electrodes. During this second phase the spark lines showed feebly. In one particular experiment it was estimated that with 80 volts applied between the electrodes the end of the first phase occurred when they were 0·05 mm. apart, the electric field at this point being 16,000 volts per cm. Such a high electric force is maintained only so long as no discharge passes. Directly the arc is established the electric force decreases rapidly. The existence of this initial intense electric field seemed to be confirmed by the broadening of the H_α and H_β hydrogen lines, observed during the early stages of the arc flash.

Hemsalech and de Gramont point out that the emission of light radiation in the arc is governed by a number of factors which generally act simultaneously, and thereby complicate the task of tracing the origin of any particular spectrum lines; but, in general, the existence of strong electric fields seems to be directly responsible for the emission of enhanced lines. These experimenters explain the "flashing up" of the lines, at the moment of striking the arc in various gaseous atmospheres, by suggesting that as the upper electrode in their experiments moves away from the stationary one a vacuous space is formed, momentarily, between the electrodes, and the initial stages of the arc discharge take

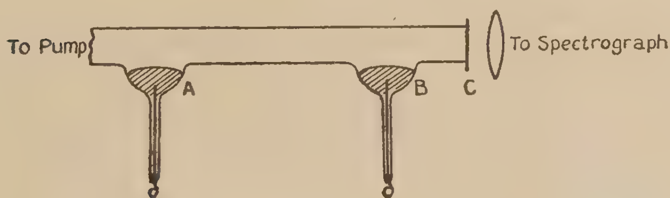
* Phil. Mag. xliii. p. 287 (1922).

place through this space. In this manner the electric field set up is enabled to develop its effect before any appreciable chemical action starts between the vapours and the surrounding gas.

Lowery *, using gold, silver and copper arcs under conditions similar to those of Hemsalech and de Gramont, found that in addition to the enhanced lines of these metals, which appeared during the initial stages of the arc flash, other lines were present which had not been observed previously. He also noted a distinct widening of the lines in the silver arc spectrum at the region near the fixed pole where, presumably, the electric fields are very intense during the early stages of the arc.

While working with the sodium–potassium alloy vapour arc lamp, which the author has described previously †, it was noticed that after the arc had been burning for some time and was then quenched, it could be restarted immediately after the cessation by applying a potential difference across the electrodes without any preliminary heating and without bringing the two liquid electrodes into momentary contact, which must be done to start the ordinary mercury vapour arc. This phenomenon can be explained by supposing the electrons and metastable atoms to persist within the lamp for an appreciable time interval after the arc had been

Fig. 1.



extinguished. It was observed, also, that the arc restarted in this manner gave an emission spectrum which was at first different from that emitted by the steady continuously burning arc. A preliminary investigation of the phenomenon was made with a type of lamp shown in fig. 1.

2. *Experiments.*

The alloy electrodes, A, B, were about 8 cm. apart; one end of the silica tube was closed by a quartz plate C, and

* Phil. Mag. xlviii. p. 1122 (1924).
† Phil. Mag. xliv. p. 944 (1922).

the other end was connected to an oil pump which, running continuously, maintained the residual gas pressure below 10^{-3} mm. Radiation from the tube was focussed by means of a quartz lens on the slit of a quartz spectrograph, and it is important to notice that in no case was the radiation from the immediate neighbourhood of either electrode incident on the spectrograph. The arc was started by warming the tube by means of a bunsen flame and passing a momentary electrodeless discharge through the vapour. After the arc had been burning for a few minutes it was stopped, and transient arc flashes produced in the tube by a mercury make and break arranged in the external circuit. In addition to this make and break the external circuit consisted of a wire rheostat, ammeter and accumulators, so that the self inductance in the circuit was very small. The applied potential difference was 80 volts, the current being 1 ampere. Arc flashes could be produced in this manner for a considerable period provided that the interval between successive flashes did not exceed 5–10 seconds.

The spectrum of these flashes differs considerably from that emitted by the steady burning arc in which, as shown in spectrogram No. I., Pl. IX., the predominant radiation is the first doublet of the principal series of sodium, λ 5890, λ 5896, the intensity of the D-lines being so great that the plate is fogged in this part of the spectrum. The lines of the two subordinate series of sodium are prominent, particularly those of the diffuse series. In the spectrum of the intermittent arc—spectrogram No. II.—the principal series lines of sodium and potassium are faint, and the subordinate series lines of sodium are almost entirely absent. The corresponding potassium lines are present and although comparatively feeble are more intense than the sodium lines. The complicated enhanced line spectra of the two metals predominate.

This characteristic spark spectrum from the intermittent arc resembles that obtained from an electric discharge tube in which one electrode was a pool of the alloy and the other an iron wire having some of the alloy coated on the end. When an electric discharge passed, very brilliant radiation was emitted from the end of the iron wire. The spectrum of this light—spectrum No. III.—is similar to that shown in spectrogram No. II.

The spectrum of the radiation emitted from the intermittent arc at high vapour pressures is given in spectrogram No. IV., and is intermediate in character between that excited by the steady and intermittent arcs at low vapour

pressures. In addition, there is a continuous spectrum which extends to λ 2100.

It may be mentioned that although the applied potential was 80 volts, this dropped to 15 volts when the arc was burning steadily, and it seems evident that the "flashing up" of the enhanced lines is explained by the relatively high potential fall which operates when the arc is started. The potential gradient in the neighbourhood of the electrodes is high, and the electrons in these parts may acquire impacting energy between successive atomic collisions sufficient to doubly ionize sodium and potassium atoms, thus giving rise to the enhanced lines.

It has been pointed out by Foote, Meggers and Mohler *, that the critical impacting energy necessary for the excitation of the enhanced lines of sodium is about 30 volts, while for potassium it is about 20 volts, but such energies are unlikely to be acquired by the bombarding electrons from the electric field except, perhaps, at the electrodes. As pointed out previously, it was not the radiation from either electrode that was focussed on the spectrograph, but light from the axial portion of the tube. Under these circumstances it is unlikely that the double ionization is effected directly by impacting energy, but it is brought about by some cumulative action. The electrons themselves acquire energy from the radiating atoms. Such collisions can occur between free electrons and atoms, in which the atom bombarded passes without emitting radiation from a stationary state of greater energy into a stationary state of smaller energy, while the impacting electron acquires an amount of kinetic energy equal to the energy lost by the atom.

Another controlling factor in the excitation of the enhanced lines in the flash arc spectrum is the phenomenon of absorption of that radiation which is emitted when the atoms resume their normal conditions. This radiation may be absorbed by any neighbouring atoms, resulting in the ejection of the electrons to temporary orbits. The excited atom thus formed may then collide with another impacting electron, which singly ionizes the atom. The radiation emitted in the first instance is probably diffused throughout the vapour in all directions, and this "photo-impact" ionization is relatively of far greater importance, especially at high vapour pressures, than ionization by successive impacts.

* Astrophys. Journ. lv. p. 145 (1922).

In the immediate vicinity of the electrodes the potential fall is high, and the electrons at this part of the arc may possess that impacting energy necessary to displace the second electron within the sodium or potassium atom. The enhanced line radiation thus produced then diffuses throughout the vapour in all directions, and is absorbed by atoms along the length of the tube. Double ionization in these excited atoms may then be completed by bombarding electrons of energy far below the theoretical values.

LXIV. *Refractivity, Ionization Potentials, and Absorption Spectra.* By R. A. Morton, *Ph.D.*, and R. W. Riding, *Ph.D.**

THE classical theory leads to a dispersion formula of the Lorenz-Lorentz type :—

$$\frac{n^2-1}{n^2+2} = \frac{C}{\nu_0^2-\nu^2} + \frac{C'}{\nu_0'^2-\nu^2} + \frac{C''}{\nu_0''^2-\nu^2} + \ldots \quad (1)$$

where n is the refractive index for light of the frequency ν, ν_0, ν', ν'', etc. are natural vibration frequencies of the absorbing entity, and C, C′, C″, etc. are constants. In gases and vapours n is practically unity, and a single term dispersion formula gives a close approximation to experimental results. Thus (1) reduces to

$$2/3 \, . \, n-1 = C/(\nu_0^2-\nu^2). \quad (2)$$

Expressed otherwise,

$$n-1 = \frac{e^2 N}{2\pi m} \cdot \frac{1}{\nu_0^2-\nu^2}, \quad (3)$$

where N is the number of electrons per cubic centimetre which are effective in dispersion. In the form

$$n-1 = \frac{N'}{\nu_0^2-\nu^2} \quad (4)$$

it is known as the Sellmeier dispersion formula.

The expression accounts for the observed dispersion of many gases †. This fact leads us to inquire into the physical significance of the frequency term ν_0. On the classical theory it should correspond to a natural vibration

* Communicated by Professor E. C. C. Baly, F.R.S.

† Cuthbertson, Proc. Roy. Soc. A, vol. lxxx. p. 411 (1908), and several later papers; Burton, *ibid.* p. 390; Koch, *Ark. f. Mat.* ix. p. 611 (1913).

frequency of the refracting entity, or in other words we should find a large absorption of radiation of the frequency ν_0. Unfortunately, the observations lead to frequencies on the short-wave side of 1200 Å., a region only amenable to investigation by means of vacuum spectroscopy. Further, the most transparent substance known, namely fluorite, ceases to transmit light below 1200 Å.

Attempts to verify the deduction that ν_0 corresponds in its physical significance with the head of an absorption band are thus bound to be very difficult. A beginning has been made by Hopfield and others by filling the entire vacuum spectrograph with gases at very low pressures. It is, however, uncertain how much significance can rightly be attached to such results from the special point of view we are considering.

Workers in the field of vacuum spectroscopy are familiar with the difficulty that the discharge is liable to spread throughout the entire apparatus. The absorption spectrum in the extreme ultra-violet is determined by illuminating the gas with a wide range of frequencies under conditions whereby excitation is not precluded, whereas the refractivity is measured for monochromatic light, using the unexcited gas. There is therefore some doubt as to the validity of attempts at correlating ν_0 with absorption measured in this way. We therefore propose to search for a substance whose dispersion may be expressed by a single- or double-term classical expression leading to the prediction of an absorption band on the long-wave side of 1200 A. The correlation can then be subjected to a rigorous test by investigating the absorption spectrum of the gas or vapour contained *in a cell* with fluorite windows. In this way the absorbing layer may be isolated from the electrical discharge of the light source, and excitation may be avoided. The present work embodies the results of some preliminary calculations.

Another line of argument may be discussed. The well-known quantum relation $h \, . \, c/\lambda = V$ enables us to express wave-lengths in terms of voltage. Expressed more conveniently,

$$\lambda(\mu) = 1{\cdot}234/V,$$

e. g. the mercury line 2537 A. $= 0{\cdot}254\,\mu = 1{\cdot}234/4{\cdot}9$ volts. It is obvious that the ν_0 terms of the Sellmeier expressions are important natural frequencies, and it would be interesting to see whether the related voltages correspond with observed voltage discontinuities. This had been done when it was discovered that we had been anticipated *. It is somewhat

* Herzfeld and Wolf, *Ann. d. Physik,* lxxvi. pp. 71–106 (1925).

startling that the calculated voltages correspond quite accurately with ionization potentials.

For the monatomic gases, ν_0 in Cuthbertson's data on helium corresponds with 507·2 Å., and the corresponding voltage is 24·33. The observed ionization potential is 24·5. For neon there is a wide discrepancy, 25·6 volts (calc.) as against 21·5 volts (obs.). For argon the values are 16·97 and 17·0 respectively. For krypton the values are 14·7 and 13·3 and for xenon 12·34 and 10·86 volts *.

Herzfeld and Wolf (*loc. cit.*) have investigated the effect of using a two-term formula :

$$n-1 = C/(\nu^2_{(\text{res.})}-\nu^2)+C'/(\nu^2_{(\text{ion.})}-\nu^2), \quad . \quad . \quad (5)$$

where $\nu_{(\text{res.})}$ and $\nu_{(\text{ion.})}$ are frequencies corresponding with resonance and ionization potentials. They come to the very interesting conclusion that the added resonance term leads to a degree of agreement with experiment which is no better and no worse than when the simple expression is used. The observations on voltage discontinuities are liable to considerable errors, so that $\nu_{(\text{res.})}$ and $\nu_{(\text{ion.})}$ must also be inaccurate. The formula is sensitive to small alterations in these terms, so that it is not surprising to find only moderately good reproduction of very accurate refractivity data. It would seem to be better to begin from refractivity and end with voltages.

These conditions also affect the work of Bergen Davis †. This author observed ‡ that the simple theory leads to a value of ν_0 for hydrogen corresponding with a potential of 16·4, which agrees fairly well with observed ionization potentials (16·0 and 16·9 volts). He then extended the formula by inserting other terms with additional ν_0 frequencies, corresponding with voltages characteristic of energy changes at levels other than the first. Some of his results may be summarized as follows :—

Substance	C.		N.		O.		S.		Cl.		Br		I.	
Voltages observed...	11·5	35	17	29·9	15·5	52	12·2	35	13·2	46	11·3	32·6	10	21
Voltages assumed in calculation.	15	35	17	29·9	18·5	25	12·2	16·2	13·2	35·3	11·3	25·8	10	13·8

* Ionization Data : Hertz, *Z. Physik*, xxviii. p. 207 (1923) ; Barton, Nature, cxiv. p. 826 (1924) ; Hertz, *Z. Physik*, xxxi. p. 470, and xxxii. p. 933 (1925).

† Phys. Rev. xxvi. p. 232 (1925).

‡ The simple Sellmeier expression of Cuthbertson, Proc. Roy. Soc. A, lxxxiii. p. 166 (1910), does not lead to 16·4 volts but 14·5 volts.

It will be observed that only in one case, that of nitrogen, are the calculated and observed voltages in agreement. The work of Herzfeld and Wolf in finding that the introduction of a second term into the dispersion formula neither improves nor worsens the degree of agreement would seem to militate against the work of Davis, and would still do so even if his calculated and observed voltages were in agreement. Davis himself writes that in the cases of helium, neon, and argon the observed potentials do not give the refractive indices if any reasonable distribution of electrons is assumed.

We have calculated the ionization potentials for the following gases from Cuthbertson's refractivity data :—

Substance.	"Dispersion" band.	$V_{(ion)}$. calc.	$V_{(ion.)}$ obs.
Nitrogen..................	725·5 Å.	17·01	17·0; 16·9; 16·3; 16·2
Hydrogen	851·8 ,,	14·5	15·8; 16; 15·8; 16·9 *
Oxygen	838 ,,	14·72	$\left.\begin{matrix}12{\cdot}5\\16{\cdot}1\end{matrix}\right\}$; 15·5; 14·0; 15·5
Carbon monoxide	899 ,,	13·72	$\left.\begin{matrix}14{\cdot}1\\15{\cdot}6\end{matrix}\right\}$; 14·3; 14·5; 15·1
Nitric oxide	859 ,,	14·3	9·3
Ammonia	1052 ,,	11·7	11·1
Carbon dioxide	800 ,,	15·04	14·3
Hydrogen sulphide ...	1070 ,,	11·3	10·4

* Richardson and Tanaka, Proc. Roy. Soc. A, cvi. pp. 640–662 (1924), give the value 14·5 volts.

The moderate agreement implies the need for a second term in the equation.

This need is emphasized by the work of Koch (*loc. cit.*). He extended the dispersion data of various gases into the ultra-violet, and although he expressed his results by means of the Cauchy formula his conclusions are relevant. With the exception of helium, the assumption of only one fundamental ultra-violet period does not account for the course of the dispersion data. The deviations are especially great in carbon monoxide and nitric oxide, in which strong additional ultra-violet absorption is found. We have seen that the employment of resonance and other potentials by Herzfeld and Wolf and by Davis does not materially assist the discussion. The development of satisfactory two-term formulæ must, therefore, apparently wait on extended data of absorption spectra in the vacuum region.

One other possibility remains to be explored, namely, the influence of absorption bands in the near ultra-violet.

The case of chlorine at once suggests itself, because of the very accurately measured absorption band in this region.

Cuthbertson's data are formulated by the expression

$$n-1 = 7{\cdot}3131 \, . \, 10^{27}/(9629{\cdot}4 \, . \, 10^{27}-\nu^2),$$

and ν_0 corresponds with 967 Å. or 12·7 volts. The observed value for the ionization potential is 13·2 volts. Mr. and Mrs. Cuthbertson themselves recognized the necessity for a second term in the equation. In order to explain how a two-term formula has been devised, it is necessary to turn to work in a quite different field.

Baly * has advanced a theory of absorption spectra which is conveniently described as centring round the molecular phase hypothesis. This hypothesis regards the natural frequencies of an absorbing entity as integral multiples of a fundamental frequency situated in the short-wave infra-red region. Accordingly (if the hypothesis is valid) any two frequencies entering into dispersion formulæ should be integral multiples of a common frequency. Hence Baly † has proposed what we shall call the Baly-Sellmeier formula:

$$(n-1)(V_1+V_2+V_3+\ldots)$$
$$= \frac{V_1N_1}{(a\nu_x)^2-\nu^2}+\frac{V_2N_2}{(b\nu_x)^2-\nu^2}+\frac{V_3N_3}{(c\nu_x)^2-\nu^2}+\ldots,$$

where ν_x is an infra-red frequency, a, b, and c are integers, $a\nu_x$, $b\nu_x$, $c\nu_x$ are those frequencies which affect dispersion. V_1, V_2, V_3 ... are the relative volumes of the absorbing entities exhibiting the frequencies $a\nu_x$, $b\nu_x$, $c\nu_x$ respectively, and N_1, N_2, N_3 ... are constants.

For chlorine, the experimental data on dispersion are reproduced extremely accurately by

$$n-1 \, . \, 350{\cdot}6 = \frac{5{\cdot}98548 \, . \, 10^{26}}{7{\cdot}873996 \, . \, 10^{29}-\nu^2}+\frac{349{\cdot}6 \, . \, 7{\cdot}96606 \, . \, 10^{27}}{104{\cdot}79487 \, . \, 10^{29}-\nu^2}.$$

The central wave-length of the first band is 3380·8 Å. (observed 3380 Å.) and the second band is at $\nu = 32{\cdot}37 \, . \, 10^{14}$

* Phil. Mag. xl. p. 15 (1920).

† Baly and Morton, Journ. Phys. Chem. xxviii. p. 659 (1924).

or 926 Å., which corresponds with 13·3 volts. Hence the observed potential of 13·2 volts is well reproduced. The expression was derived from refractivity data only, and the assumptions of the phase theory are not essential from the special point of view of this paper. The essential fact is that an equation has been arrived at which

(*a*) very accurately reproduces the data;

(*b*) employs the frequency of an accurately measured absorption band in the near ultra-violet;

(*c*) leads to a frequency in the extreme ultra-violet which is very much closer to the value calculated from the ionization potential than that obtained from the simple dispersion formula.

This result leads us to place some reliance on the correlation of ionization potential with a dispersional frequency. It also seems to justify an attempt to measure absorption spectra in the region 1200–1800 Å. with a view to confirming these views.

It may be asked why the dispersional frequency should be related in any way to the ionization potential. Except that both phenomena are concerned with outer electrons, no answer can be made. The dispersion equations are of classical origin, whereas the conversion of voltages into frequencies is made by quantum assumptions, so that the reconciliation of the wave theory and the quantum theory is somehow involved.

It would also seem that if with photoactivation of chlorine there is a concomitant change in physical properties, the illumination of chlorine with ultra-violet light to as far as $\lambda=1200$ Å. (using a fluorite window) should result in a change of refractive index large enough to be measured interferometrically.

We express our thanks to the United Alkali Company, who, by the most generous terms of appointment, have enabled one of us (R. W. R.) to undertake experimental work on the above lines for one year at the University of Liverpool.

LXV. *The Absorption Spectra of the Vapours of* Zn, Cd, Pb, Sn, Bi, *and* Sb. *By* JOHN G. FRAYNE, *Ph.D.*, *and* ALPHEUS W. SMITH, *Ph.D.**

[Plate X.]

IN a recent paper by Zumstein † a new kind of absorption cell is described. The cell is a graphite tube open at both ends, the bead of metal under observation being placed in the centre of the tube. An oxy-acetylene torch is used to vapourize the metal. All previous absorption cells have had quartz windows at both ends in order to allow the ultra-violet light to pass through, at the same time making it possible to evacuate the apparatus. The deposition of the metal on the windows was a serious handicap in this type of apparatus. Further, it was impossible to heat such a cell above 1150° C., the softening point of fused quartz.

The present research was undertaken by the authors to test the feasibility of using this new type of cell for metals of low melting points. Cadmium was first investigated and gave positive results on the first spectrogram. Wood and Guthrie ‡ had previously investigated the absorption spectrum of this element and had found two heavy absorption lines. Absorption in zinc vapour has been studied by McLennan and Edwards §. Grotrian ‖ has made a study of absorption in lead vapour, finding twelve lines in the ultra-violet. While this research was in progress, Zumstein¶ published a paper on lead absorption in which he states that thirty lines were absorbed in the ultra-violet. McLennan, Young and McLay** have studied the absorption spectrum of tin. They used the evacuated quartz tube and arc reversal methods. Grotrian†† has found the line λ 3067 strongly absorbed in Bi vapour and also found band absorption at high temperatures. Ruark, Mohler, Foot and Chenault ‡‡ have studied the emission and absorption spectra of metals in Group V. of the Periodic

* Communicated by the Authors.

† Zumstein, Phys. Rev. xxv. p. 523 (1925).

‡ Wood and Guthrie, Astrophys. Journ. xxix. p. 211 (1909).

§ McLennan and Edwards, Phil. Mag. xxx. p. 695 (1915).

‖ Grotrian, *Zeit. fur Phys.* xviii. p. 169 (1923).

¶ Zumstein, Phys. Rev. xxvi. p. 189 (1925).

** McLennan, Young and McLay, Trans. Roy. Soc. Can. xviii. p. 57 (1924).

†† Grotrian, *Zeit. fur Phys.* xviii. p. 169 (1923).

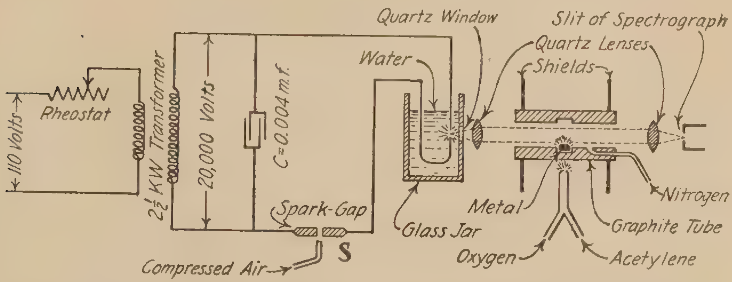
‡‡ Ruark, Mohler, Foote and Chenault, B. S. Sci. Papers, 490, p. 468 (1924).

Table. They found band and line absorption in Bi and band absorption in Sb vapour.

Experimental Procedure.

The arrangement of apparatus (fig. 1) was similar to that used by Hulbert *. A condensed spark under water was used as a source of continuous radiation. A condenser of capacity 0·004 m.f. was charged by means of a 20 kv. $2\frac{1}{2}$ kw. transformer and discharged through an auxiliary spark gap S, and an under-water spark gap in series. To insure an abrupt discharge compressed air was forced between the terminals of the auxiliary spark gap. Tungsten rods, 3·5 mm. in diameter, and ground to knife edges, served as electrodes for the under-water gap. The radiation from

Fig. 1.



the under-water spark passed directly through the quartz window in the side of the glass jar and then through two quartz lenses, by means of which it was brought to a focus on the slit of the spectrograph. The spectrum thus obtained was continuous except for occasional absorption lines and extended to about 2100 A.

The graphite tube was about 15 cm. long and had a hole 1·7 cm. in diameter drilled through the centre with a small pocket in the middle to hold the metal under investigation. Through a side tube nitrogen flowed into the graphite tube and thus prevented oxidation of the metal. The central portion of the graphite tube was heated from the outside by means of an oxy-acetylene torch. In this way a sufficient quantity of the metal was vapourized to give satisfactory absorption spectra. Iron shields protected the source of light and the spectrograph from the flame. In the case of some of the metals with lower melting points oxygen and natural gas were substituted for oxygen and acetylene.

* Hulbert, Phys. Rev. (2) xxiv. p. 129 (1924).

A Féry spectrograph was used throughout the research. In this instrument the collimator and camera lenses are suppressed. The only optical part is the prism, which is traversed by the radiation twice in opposite directions. The curvature of the front and back surfaces of the prism is such that a sharp spectrum is obtained on a photographic film which is bent in the form of a cylindrical surface. The spectrum extends from 2100 Å to 8000 Å and has a length of about 22·4 cm. Eastman Kodak super-speed films were used and were found quite satisfactory. Below 2400 Å the radiation was weak and the films were also less sensitive.

The wave-lengths of the absorption lines were usually found by comparison with the emission spectra. The arc and spark spectra were usually photographed on the same film as the absorption spectra.

Experimental Results.

Zinc.

The line λ 3076, $1S-2p_2$, was strongly absorbed at temperatures around 700° C. The line λ 2139, $1S-2P$, which had been observed by McLennan and Edwards, failed to appear as an absorption line in any of the eighty exposures. The Cd line λ 2288, $1S-2P$, appeared on all the zinc photographs. The emission spectrum of the Zn was compared with that of Cd, and it was found that the latter line appeared on both spectrograms. No other Cd line was present in the Zn spectrum. Lead was present as an impurity to the extent of ·001 per cent. and the fundamental Pb line λ 2833 was strongly absorbed. Fig. 2 (Pl. X.) represents the absorption spectrum of Zn.

Cadmium.

The results obtained with Cd corroborate the work of Wood and Guthrie on this metal. The two fundamental lines λ 3261, $1S-2p_2$, and λ 2288, $1S-2P$, were strongly absorbed. At high temperatures the latter line widened out into a band nearly 20 Å wide. The line λ 3261 appeared at about 600° C. and remained sharp as the temperature was raised. The zinc line $1S-2p_2$ appeared on some of the negatives. Fig. 2 (Pl. X.) represents the absorption spectrum of Cd.

Tin.

The following lines appeared in the Sn absorption spectrum: $\lambda\lambda$ 3009, 2863, 2707, 2483, 2209 and 2171. The

absorption lines in this metal were not nearly so pronounced as in the metals discussed above. The first three listed were observed by Grotrian and the others have been observed as absorption lines by McLennan, Young and McLay.

Lead.

In addition to the line λ 2833, which was found as an impurity in the zinc spectrum, the following lines appeared on the spectrograms :

Wave-length.	Series Notation.
4058 A	$2p_2-2s$
3684	$2p_3-2x$
3640	$2p_3-2s$
3262	$2p_1-4d_3$
3240	$2p_1-4d_2$
2873	$2p_2-3d_3$
2823	$2p_2-3d_2$
2802	$2p_2-3d_1$
2663	$2p_2-X_2$
2614	$2p_3-3d_2$
2446	$2p_3-3s$
2247	$2p_3-4d_2$
2170	$2p_4-3d_2$

The above notation is taken from Grotrian's paper referred to above. The normal state of the lead atom corresponds to the $2p_4$ level. The $2p_1$, $2p_2$, $2p_3$, $2p_4$, are metastable states. The lines λ 2833, $2p_4-2s$ and 2170, $2p_4-3d_2$, which originate from the $2p_4$ level, are easily absorbed at low temperatures and widen into bands as the temperature is raised. The lines from the metastable states appear at higher temperatures. It is of interest to point out that Zumstein failed to observe the lines λ3260 and λ3240, which originate from the $2p_1$ level. Grotrian had previously observed these two lines in the lead absorption spectrum.

Bismuth.

The Bi absorption spectrum is much more complicated than that of any of the preceding metals in that it consists of lines and bands. In the ultra-violet the lines λ 3067, $3d_2-\alpha$, λ 2276, $3d_2-\delta$, λ 2230, $3d_2-\epsilon$, λ 2228, $3d_2-\zeta$, were strongly absorbed. In the visible, the line λ 4254, $\alpha-\xi$, was absorbed. Two other absorption lines appeared in the ultra-violet which correspond to the Sb lines λ 2293 and

λ 2475. However, as no line absorption was detected in Sb vapour it is doubtful if these are true Sb lines. At low temperatures a series of channelled bands appeared, extending from 2880 Å to 2670 Å. These bands merged into one continuous band as the temperature was raised. Another band appeared below 2200 Å at low temperature and extended with rising temperature to about 2500 Å. Another typical band appeared in the visible. This band consisted of two strong absorption lines with finer lines on either side. One of these lines corresponded to the emission line λ 4254, as noted above. A typical spectrogram is reproduced in fig. 2 (Pl. X.). The lines λ 2230 and λ 2228 do not reproduce as they are within the region of the band. When a larger bead of metal was heated dense clouds of vapour emanated from the cell and the absorption appeared as represented in fig. 2 (Pl. X.) (lower spectrum).

Antimony.

No line absorption was detected in Sb vapour. At low temperatures an absorption band appeared below 2200 Å and extended into the visible with increasing temperature. This result is in accord with the photographs published by Dobbie and Fox *.

Discussion.

In the metals of Group II. of the Periodic Table the 1S is the lowest energy level, the 2P being the next lowest. Consequently, atoms of the normal vapour will have their valence electrons in the 1S level and on excitation from some external source will permit them to transfer to the neighbouring 1P level. If the removal is brought about by the absorption of radiant energy, an absorption line of wave number $\nu = \frac{W_1 - W_2}{h}$ should appear. W_1 is the energy associated with the 1S and W_2 that of the 2P level, and h is Planck's constant. Similarly, removal of an electron from the 1S to the $2p_2$ level should give rise to a corresponding absorption line.

The results obtained in Cd vapour are completely in accord with the theory. The 1S—2P line was strongly absorbed at low temperatures. It also appeared in the absorption spectra of several other metals where Cd was present as an impurity of less than ·001 per cent. The

* Dobbie and Fox, Proc. Roy. Soc. A, xcviii. p. 147 (1920).

combination line $1S-2p_2$ appeared at a higher temperature than the former, but was very prominent.

The results obtained with Zn vapour were not so satisfactory. The line $1S-2p_2$ was very strongly absorbed but $1S-2P$ was not detected. As was pointed out above, the Cd line $1S-2P$ appeared on all the Zn negatives. There is a possibility that this line 2288 A may be a zinc line as well as a Cd line. It is doubtful, however, that it should be a resonance line for both metals. It is of interest to point out that Tate * found a resonance potential of 5·65 volts for zinc, whereas the calculated value based on λ 2139 is 5·77 volts. If λ 2288 were a resonance line of zinc there should be a corresponding resonance potential of 5·4 volts.

The Pb line λ 2833 is unquestionably a resonance line for that element. It occurs as an impurity in the absorption spectra of other metallic vapours, and is the most prominent line in the Pb absorption spectrum. It is usually accompanied by λ 2170, which also arises from the $2p_4$ or lowest level of the Pb atom.

Resonance and ionization potential measurements have been made on metals of Group V. by Foote, Rogulev and Mohler †. Their results show that λ 4722 and λ 3067 are fundamental lines in the Bi spectrum. The latter line has been observed as an absorption line by Grotrian and others. The other line has so far failed to be detected in any absorption experiments. The lines $\lambda\lambda$ 2276, 2230, and 2228, which were observed by the authors, correspond to electron transfers from the lowest level, $3d_2$, to the δ, ϵ, ζ levels respectively. The line λ 4254, which was observed by the authors, corresponds to a transfer from the α to the ξ level.

Band absorption predominates in Sb vapour. In the series arrangement worked out for this metal by Ruark, Mohler, Foote and Chenault, the lines $\lambda\lambda$ 2311 and 3232, arising respectively from the $3d_2$ and $3D_1$ levels, are the fundamental lines of the element. However, there is no trace of absorption of either line.

Sept. 12, 1925.

Note added to MS. on Oct. 2.—In the September issue of the Phil. Mag. an article appeared on "Absorption of Light by Vapours of Pb, Sn, Bi, Sb and Mg," by Prof. Narayan and Mr. Rao. They found absorption lines in Sb vapour, including the "raie ultime" λ 2311.

* Tate, Phil. Mag. xxxvi. p. 64 (1918).

† Foote, Rognley and Mohler, Phys. Rev. xiii. p. 59 (1919).

LXVI. *The Wave Form of the Current in an Electrically Maintained Tuning-fork Circuit.* By V. H. L. Searle,

M.Sc., Assistant Lecturer in Physics, University College of the South-West of England, Exeter *.

[Plate XI.]

I. *Introduction.*

In view of the frequent use which is made of the electrically maintained tuning-fork as a standard of frequency it was thought that some interest would attach to an investigation of the form of the current which flows through such a circuit and of the purely electrical factors which exercise decided influence on the current form. Incidentally it was hoped to define, in rather more detail than is possible with frequency measurements, the degree of uniformity of vibration impulse which the various methods possess. The experiments, therefore, had the two-fold aim of comparing different methods of maintenance with one another and the detailed examination of the factors influencing each. This aim has not yet been carried out in its entirety, but the present work gives the results so far obtained and they indicate that further research might disclose interesting facts.

The two circuits which have been studied may be described, for the sake of reference, as the "solid contact" and "mercury break" circuits. By the former is meant the usual method of make and break which employs a platinum-ended screw which, by its intermittent contact with a platinum boss on a small brass piece attached to the fork prong, produces the necessary current variations. By the second, reference is made to the periodic current interruptions due to the withdrawal, by reason of the prong movement, of a platinum wire from the surface of a pool of mercury which acts as one of the current leads. This form of interruption was suggested by Helmholtz and, as will be shown, has a uniformity of action greatly surpassing that of the "solid contact" method.

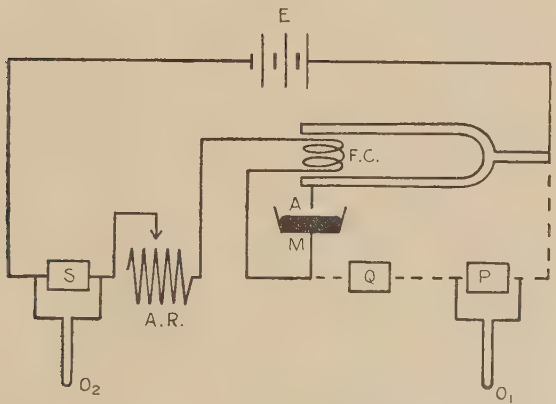
II. *Experimental Results.*

In both investigations the form of circuit shown in fig. 1 was used. E was a 6-volt accumulator which supplied current through an adjustable resistance A.R., a shunt S

* Communicated by Prof. F. H. Newman, D.Sc.

placed across the oscillator O_2 of a Duddell oscillograph, the make and break contact AM and the coil FC of the fork which had a frequency of 256. The platinum-mercury contact consisted of a wire 12 mm. in length and 0·37 mm. diameter soldered to the fork prong and dipping into a pool of mercury, about 5 mm. deep and 50 mm. across, which was contained in a wooden vessel whose position was adjustable by means of a rising table. Direct current not being available, the mirror of the vibrator O_2 was illuminated by an alternating arc which was found to work much more steadily when, by means of a transformer, the pressure was reduced to 30 volts. The current through the arc was controlled by an iron wire rheostat and, when conditions

Fig. 1.



were favourable for an exposure, this resistance was temporarily cut out and the plate released in the photographic chamber of the oscillograph. In this way a sufficiently brilliant spot of light was obtained to give good density in the negative.

The current form obtained by the "solid contact" method of interruption is shown in Pl. XI. No. I. The arrow indicates the direction of movement of the falling plate, and thus the rise of current, or "make," is distinguished by that ordinate of a crest which is first traced out. It will be noticed that the current builds up rapidly and practically uniformly to its peak value, but that the "break" is rapid at first and then more gradual, causing curvature at the bottom of the wave. Secondly, complete establishment of the maximum current value does not occur at each vibration of the fork

owing to imperfect contact of the platinum points. The same effect causes the small current tremors distinctly noticeable at one of the imperfect contacts, these tremors being due to a rapid vibration of the brass strip carrying the platinum boss. In all the photographs in the plate the periodic changes in the thickness of the lines and the corresponding bands of light across the prints are due to the intensity fluctuations of the arc.

In view of the local irregularities in the "solid contact" wave form attention was directed to the mercury-platinum break, and the current form in the plain circuit of the diagram is shown in No. II. of the Plate. It is immediately noticeable that in this case rather surprising regularity of current variation is obtained, and the result of all experiments with this form of interruption may be here anticipated by the remark that in no instance was a lack of regularity observed. An examination of the wave form shows that, with the mercury break, the "make" is not now linear but proceeds rapidly at first and then more slowly until the peak value is reached. The "break" follows practically the same law as in the mechanical interrupter case. This similarity is probably due to the fact that in both cases an arc is struck and its presence helps to maintain the current—which never drops to a zero value—in the same way.

It was first expected that the mercury break, alone, would be ineffective owing to the agitation of the mercury surface and to the excessive arcing which takes place on "break," but, in practice, it was found that the maintained vibration was exceedingly easy to set up and would continue without attention for long periods—twenty minutes was the longest time actually employed, and in this case the vibration was stopped arbitrarily. The interruption owes its regularity to the forcing, on the mercury surface, of coperiodic stationary ripples so that, at each descent of the platinum point, the conditions of the previous contact are exactly reproduced. It was also noticed that, as the contact point rose from the mercury a ripple crest followed it. The amplitude of the liquid surface immediately below the point was, however, smaller than that of the prong, so the current-strength variation was due to a changing length of mercury arc as well as to a varying degree of ionization.

Since the different characters of the "make" in No. I. and No. II. of the Plate are attributable to the mercury arc, it was anticipated that a condenser across the gap would reproduce the previous form of "make." When the gap was thus shunted it was noticed that the peak value of the

current amplitude decreased and at the same time the current was more nearly completely interrupted. This, of course, would be expected since the condenser practically eliminates the conducting path of the arc. An examination of the corresponding wave form No. III. in the Plate shows that the "make" curve is much more nearly linear while the curvature of the "break" is enhanced. The general property of complete regularity, however, is conserved. It was also found that, contrary to expectations, this circuit showed no superiority over the "plain" circuit in ease of maintenance. Indeed, for easy working, it was advisable to commence the vibration as in the previous case and then to bring in the condenser by means of a plug-key.

The second modification which suggested itself was the introduction into the circuit of an additional source of inductance, and several coils were used varying from a simple air coil of about 50 turns to an iron-cored coil of about 150 turns all on 1 centimetre diameter formers. The only effect noticed was an increased difficulty of maintenance, for no great variation in the current wave form was obtained. This is shown in the companion curves No. IV. *a* and No. IV. *b* of the Plate, in which No. IV. *a* shows the current form when an open cored coil is used, and No. IV. *b* represents the same circuit after the introduction of a soft iron core of $12\frac{1}{2}$ cm. length and 1 cm. diameter. Comparison of these two curves shows no variation of any moment and, in addition, the shape is the same as No. II. of the Plate. [The change of amplitude is of no significance since this was a result of a change in the ohmic value of the circuit.] It will be shown later by a Fourier analysis of the curve, that the amplitudes of all the harmonics in the current wave form are of small and quickly decreasing values, and thus the effect of additional inductance is confined chiefly to the production of an increased lag angle without material modification of the wave form.

In a final attempt to introduce factors which might be expected to produce deformations in the current form a combination of capacity and inductance was included, the capacity being across the gap and the inductance in series with the rest of the circuit and being additional to that of the fork coil. This modification changed the wave form of the current as can be seen in No. V. *a*, No. V. *b*, and No. V. *c* of the Plate. The inductance was kept constant while the capacity changed progressively. This produced a similarly gradual change in the small deformations which are shown in these photographs. The three typical results

given indicate the change accompanying a variation of capacity from 0·5 to 1·5 m.f.d. It will be noticed that in No. V. *a* there are two local oscillations occurring in the "break" but none in the "make." This indicates that the augmentation of the current which accompanies the rapid reduction in the mercury-gap resistance is sufficient to mask any tendency for the tuned circuit to produce local oscillations, but that on the "break" these oscillations, though small in magnitude, are not completely masked. Comparison between No. V. *a* and No. V. *b* shows an increase in the amplitude of the deformation together with a later occurrence such that the second oscillation now occupies practically the position between "make" and "break." This progression becomes even more manifest in No. V. *c*, where the second oscillation has disappeared and only one kink in the curve is seen, this, however, being of relatively large amplitude. It will be noticed that, while it has been found possible materially to affect the current form, the change is quite definite and the mercury break continues to act with perfect regularity.

III. *Discussion of Results.*

If E is the E.M.F. of the accumulator, R_1 the ohmic resistance of the circuit without the mercury-platinum break, L the coefficient of self-inductance of the fork coil, R the ohmic resistance of the gap, and the current i is connected with the time by the relation $i=f(t)$, then the equation connecting these quantities is:

$$L\frac{d}{dt}f(t)+f(t)[R_1+R]=E, \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

and a knowledge of L, $f(t)$, E, and R_1 suffices to determine R which will also be a function of the time. E and R_1 are easily obtained, while $f(t)$ and L were measured as follows.

To determine $f(t)$ the 12-ordinate scheme, for a Fourier analysis, of C. Runge * was employed. A travelling microscope measured the distance between two successive positions on the negative of minimum current value, and this length was divided into twelve equal parts by points $y_0, y_2, y_2 \ldots y_{12}$. The curve ordinates at these points were measured and arranged as shown in Table I.

* C. Runge, *Zeits. f. Math. und Phys.* xlviii. p. 443 (1903).

TABLE I.

Values of Ordinates	2·65	3·04	3·37	3·62	3·35	2·19	1·41
		2·01	1·06	0·45	0·55	0·86	
Sums	2·65	5·05	4·43	4·07	3·90	3·05	1·41
Differences		1·03	2·31	3·17	2·80	1·33	
	2·65	5·05	4·43	4·07	1·03	2·31	3·17
	1·41	3·05	3·90		1·33	2·80	
Sums	4·06	8·10	8·33	4·07	2·36	5·11	3·17
Differences	1·24	2·00	0·53		−0·30	−0·49	
	4·06	8·10			2·36	1·24	
	8·33	4·07			3·17	0·53	
Sums	12·39	12·17			−0·81	0·71	

Multipliers.	Sine Terms.					Cosine Terms.						
	1st.	5th.	2nd.	4th.	3rd.	1st.	5th.	2nd.	4th.	3rd.	0.	6th.
0·5	1·18					0·27		−4·17	4·05			
0·866		4·43	−0·26	−0·42			1·73					
1·00	3·17				−0·81	1·24		4·06	−4·07	0·71	12·39	12·17
1st Column.	4·35		−0·26		−0·81	1·51		−0·09		0·71	12·39	
2nd "	4·43		−0·42			1·73		−0·02			12·17	
Sums	8·78		−0·68		−0·81	3·24		−0·11		0·71	24·56	
Differences.	−0·08		0·16			−0·22		−0·07			0·22	
	$A_1=$	1·46	$A_2=$	−0·11	$A_3=$	$B_1=$	0·54	$B_2=$	−0·02	$B_3=$	$A_0=2·05$	
	$A_5=-0·01$		$A_4=$	0·03	−0·81	$B_5=-0·04$		$B_4=$	−0·01	0·12	$B_6=0·02$	

We thus have for $f(t)$ to a first approximation and making a suitable choice of the point $t=0$,

$$i = 2·05 + 1·56 \sin pt.$$

These values are in cms., and to transform them into amperes a calibration of the oscillograph had to be made. This yielded the result:

1 cm. ordinate represented 0·1144 amp.

Thus i, expressed as amps., becomes:

$$i = 0·235 + 0·177 \sin pt.$$

The ordinary bridge methods of measuring inductance are not easy to apply in the case of a small iron-cored coil. It was therefore decided to use the oscillograph for this purpose. To do this the main lighting current of 60 cycles A.C. was used and a circuit was arranged as shown in fig. 2. The resistances R and r provided a means of adjusting the P.D. between M and N, and thus of regulating the current value through the fork coil F C. This current was measured by using the vibrator O_2. The P.D. across FC was recorded by the second oscillator O_1 in series with which was a resistance X large compared with that of FC. The falling

Fig. 2.

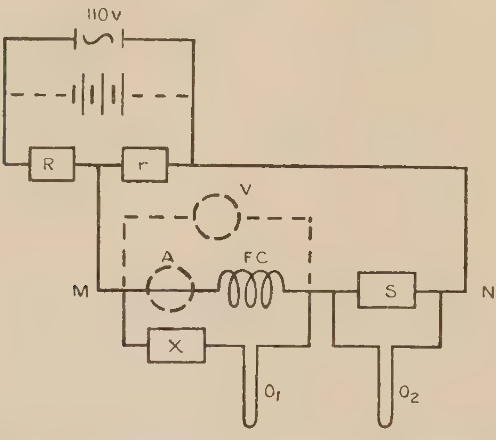


plate thus registered P.D. and current, as is shown in No. VI. of the Plate, the greater amplitude curve being the current form.

To calibrate these curves the circuit was rearranged as shown by the dotted additions in fig. 2. The mains were replaced by a 6-volt accumulator, and a voltmeter V and an ammeter A were inserted. This gave two displaced straight lines on the falling plate, and the readings of A and V provided calibration values for the 60-cycle curves.

The value of the inductance L was measured by the use of each of the two formulæ :—

$$I = \frac{E}{\sqrt{R^2 + (2\pi n L)^2}}, \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

$$\tan\phi = \frac{2\pi n L}{R}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

where I is the maximum current value, E the maximum

P.D., R the ohmic resistance of FC, n the frequency of the current, and ϕ the angle of lag.

The values obtained were :

$$I = 0{\cdot}192 \text{ amp.} \qquad E = 0{\cdot}883 \text{ volt.}$$
$$R = 4{\cdot}48 \text{ ohms.} \qquad n = 60, \quad \phi = 13^{\circ}{\cdot}2.$$

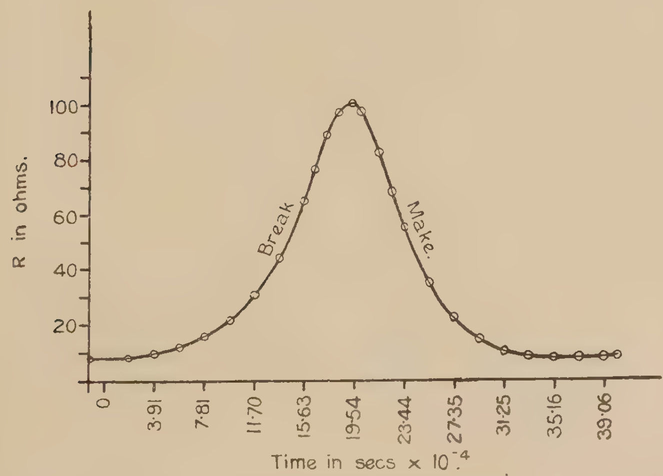
From equation (ii.) we have $L = 0{\cdot}0028$ henry.
From equation (iii.) $L = 0{\cdot}0028$ henry.

If values of L, $f(t)$, R_1, and E are substituted in equation (i.) it becomes

$$R = \frac{6{\cdot}36 - 0{\cdot}767 \cos pt}{0{\cdot}235 + 0{\cdot}177 \sin pt} - 8{\cdot}78. \quad . \quad . \quad . \quad \text{(iv.)}$$

This equation indicates how the resistance of the mercury arc varies with time, and when graphed gives the curve

Fig. 3.



shown in fig. 3. Thus the mercury-arc resistance curve is not symmetrical about the maximum ordinate, or in other words the resistance for a given arc length is different on the "make" from on the "break."

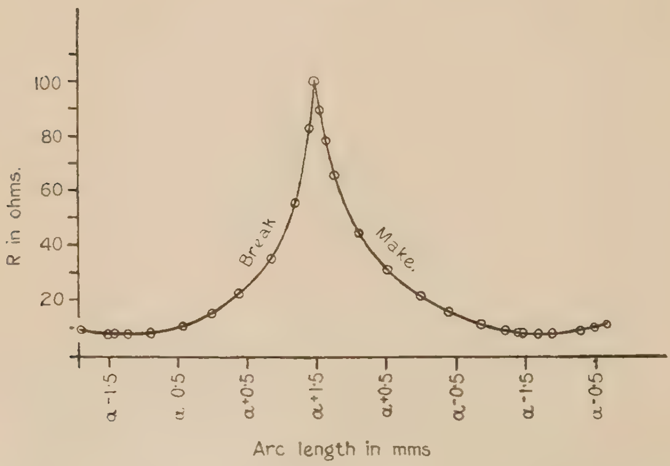
It is an easy matter from this graph to deduce the curve connecting the arc resistance with arc length, since the latter is a known function of the time. It has been stated that the mercury surface oscillates in unison with the fork but with smaller amplitude. The arc length is thus the difference between two expressions of the form $a + b \sin pt$ and $c + d \sin pt$, and is given by $l = \alpha - \beta \sin pt$, where $(\alpha - \beta)$

measures the minimum and $(\alpha+\beta)$ the maximum separation of the platinum wire from the instantaneous position of the surface immediately beneath it: $(\alpha-\beta)$ was small but not zero, and β was of the order 1·5 mm. Using this value for β—a change merely alters the scale of the graph—the connexion between arc length l and resistance R is obtained by eliminating t between equation (iv.) and the equation

$$l=\alpha-1\cdot5\sin pt.$$

The result of this elimination gives two values of R for a single value of $(\alpha-l)$; *i. e.*, again it is seen that the "make" resistance for a given arc length differs from the "break" resistance for the same length. The graph connecting R and l is shown in fig. 4.

Fig. 4



It was finally hoped to obtain some check on these results by a combined P.D. and current curve for the circuit examined above. For this the arrangement was as in fig. 1 with the additions shown dotted. The resulting trace is shown in No. VII. of the Plate, and discloses the reciprocal rise of P.D. and fall of current consequent on the changing resistance. This curve, however, could not usefully be calibrated as it was found necessary, in order to obtain a reasonable P.D. amplitude, to have the O_1 vibrator circuit

across the gap of resistance comparable with that of the gap itself. The conditions in this case are, therefore, not strictly comparable with the investigated case.

IV. *Summary.*

(i.) Records of the current form in electrically maintained fork circuits were obtained by means of the Duddell oscillograph, and it was found that the "solid contact" means of maintenance acts irregularly. The "mercury-platinum" break—in which a platinum wire fixed to the fork prong dips into, and out from, a mercury surface—however, is very regular and extremely easy to work.

(ii.) Capacity across the spark-gap reduces the current amplitude and affects the shape of the current curve. Inductance does not affect the wave form, but renders maintenance more difficult.

(iii.) By means of a Fourier analysis of the curve and measurement of the constants of the circuit, the variation of mercury arc resistance with time and with arc length has been investigated.

(iv.) The general deductions from (iii.) above are verified by a combined current and potential oscillogram.

V. *Description of Plate.*

No. I. Current wave form with "solid contact" method of make and break.

No. II. Current wave form with "mercury-platinum" method of make and break.

No. III. Same as II., but showing the effect of a condenser across the spark-gap.

No. IV. *a* and No. IV. *b*. Same as II., but showing the effect of an additional source of inductance—IV. *a* without, and IV. *b* with, an iron core.

No. V. *a*, No. V. *b*, and No. V. *c*. Show the effect of a combination of capacity and inductance. The inductance is constant, and the capacity ranges from ·5 mfd. to 1·5 mfd.

No. VI. P.D. and current curves for a 60-cycle A.C.

No. VII. P.D. and current curves for the circuit used in No. II.

In conclusion the author would like to express his thanks to Prof. F. H. Newman for suggesting this investigation.

LXVII. *The Application of the Rigorous Quotient Theorem.*

By ALEXANDER BROWN, *Professor of Applied Mathematics, University of Cape Town* *.

§ 1. IN Tensor Theory considerable use is made of the 'Rigorous Quotient Theorem,' viz.: "A quantity which on inner multiplication by *any* covariant (or *any* contravariant) tensor always gives a tensor is itself a tensor." Attention is here called to the need that the multiplying tensor be completely arbitrary. If the tensor used in forming the product be in any way restricted the theorem cannot be used; but in certain cases other inferences may be made. This is illustrated below by reference to cases where apparently incorrect application has been made of the theorem, and to conclusions that can be drawn in particular cases where the tensor used is not perfectly arbitrary.

§ 2. In finding the covariant derivative of a tensor one of the conditions we have to satisfy is that the quantity sought is a three-rank tensor. Eddington ('Math. Theory of Relativity,' § 30) uses the Rigorous Quotient Theorem for this purpose thus: differentiate the invariant

$$A_{\mu\nu}\frac{dx_\mu}{ds}\cdot\frac{dx_\nu}{ds}$$

along a geodesic and substitute for $\dfrac{d^2x_\mu}{ds^2}$ from the geodesic equation; we then find the invariant expression

$$\frac{\partial A_{\mu\nu}}{\partial x_\sigma}\cdot\frac{dx_\sigma}{ds}\cdot\frac{dx_\mu}{ds}\cdot\frac{dx_\nu}{ds}-A_{\mu\nu}\{\beta\gamma,\mu\}\frac{dx_\beta}{ds}\cdot\frac{dx_\gamma}{ds}\cdot\frac{dx_\nu}{ds}$$
$$-A_{\mu\nu}\{\delta\epsilon,\nu\}\frac{dx_\delta}{ds}\cdot\frac{dx_\epsilon}{ds}\cdot\frac{dx_\nu}{ds}. \quad (1\cdot1)$$

In this expression all the suffixes are dummy suffixes and can be changed and interchanged in various ways. Leave the first term in (1·1) as it is; in the second change μ into α, β into μ, and γ into σ; and in the third change ν into α, δ into μ, and ϵ into σ; (1·1) now becomes

$$\left(\frac{\partial A_{\mu\nu}}{\partial x_\sigma}-\{\mu\sigma,\alpha\}A_{\alpha\nu}-\{\nu\sigma,\alpha\}A_{\mu\alpha}\right)\frac{dx_\mu}{ds}\cdot\frac{dx_\nu}{ds}\cdot\frac{dx_\sigma}{ds}; \quad (1\cdot2)$$

* Communicated by Prof. A. S. Eddington.

and it is inferred that the coefficient

$$A_{\mu\nu\sigma} \equiv \frac{\partial A_{\mu\nu}}{\partial x_\sigma} - \{\mu\sigma, \alpha\} A_{\alpha\nu} - \{\nu\sigma, \alpha\} A_{\mu\alpha}$$

is a 3-rank covariant tensor by application of the Rigorous Quotient Theorem.

It appears, however, that the reasoning here is not legitimate. The *result* obtained is correct, as can be verified by direct transformation; but this correct result is only one out of several that can be obtained by identical reasoning, and it appears an accident that the true result has been chosen instead of one of the false ones.

To get (1·1) into a form suitable for the application of the Rigorous Quotient Theorem we must transform the sets $\beta\gamma\nu$ and $\delta\epsilon\mu$ each into $\mu\nu\sigma$. For the former of these, six methods of substitution are possible which, with the corresponding factors, are tabulated below :

β.	γ.	ν.	Factor.
σ	μ	ν	$A_{\alpha\nu}\{\sigma\mu, \alpha\}$
σ	ν	μ	$A_{\alpha\mu}\{\sigma\nu, \alpha\}$
μ	σ	ν	$A_{\alpha\nu}\{\mu\sigma, \alpha\}$
μ	ν	σ	$A_{\alpha\sigma}\{\mu\nu, \alpha\}$
ν	μ	σ	$A_{\alpha\sigma}\{\nu\mu, \alpha\}$
ν	σ	μ	$A_{\alpha\mu}\{\nu\sigma, \alpha\}$

. . . (1·3)

We get the same set precisely from the third term of (1·1). Hence

$$\left(\frac{\partial A_{\mu\nu}}{\partial x_\sigma} - J - K\right) \frac{dx_\mu}{ds} \cdot \frac{dx_\nu}{ds} \cdot \frac{dx_\sigma}{ds}$$

is an invariant where J and K are any of the six factors in (1·3). If the Rigorous Quotient Theorem were applicable, we should conclude that $\frac{\partial A_{\mu\nu}}{\partial x_\sigma} - J - K$ was a 3-rank tensor, which, as a matter of fact, is not the case for some groupings of the J's and K's.

§ 3. The reason why the Theorem is not applicable here is that one of its conditions is not fulfilled ; $\frac{dx_\mu}{ds} \cdot \frac{dx_\nu}{ds} \cdot \frac{dx_\sigma}{ds}$ is not an *arbitrary* 3-rank tensor ; it is a special tensor—the outer product of three vectors, and it is familiar that an *arbitrary* 3-rank tensor cannot be expressed as the outer product of three vectors. From another point of view it

has only 20 distinct elements instead of the 64 belonging to the arbitrary tensor of this rank.

§ 4. To find what inferences can be drawn from the invariance of quantities like (1·2), it is necessary to retrace the steps in the proof of the Rigorous Quotient Theorem.

As a simple case suppose we are given that

$$A_{\mu\nu} \,.\, dx_\mu \,.\, dx_\nu \text{ is invariant,} \quad . \quad . \quad . \quad (2\cdot1)$$

i.e.
$$A'_{\alpha\beta} \,.\, dx'_\alpha \,.\, dx'_\beta = A_{\mu\nu} \,.\, dx_\mu \,.\, dx_\nu$$
$$= A_{\mu\nu} \cdot \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \,.\, dx'_\alpha \,.\, dx'_\beta.$$

$$\therefore \quad \left(A'_{\alpha\beta} - \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \,.\, A_{\mu\nu}\right) dx'_\alpha \,.\, dx'_\beta = 0. \quad . \quad (2\cdot2)$$

In this, the elements $dx'_\alpha \,.\, dx'_\beta$ are not all independent; thus $\alpha=1$, $\beta=2$ and $\alpha=2$, $\beta=1$ give the same element; so that we cannot say that the coefficient belonging to $\alpha=2$, $\beta=1$ vanishes but only that the sum of the coefficients belonging to $\alpha=2$, $\beta=1$ and $\alpha=1$, $\beta=2$ vanishes.

Hence from (2·2) we deduce, if α and β are the same,

$$A'_{\gamma\gamma} = \frac{\partial x_\mu}{\partial x'_\gamma} \cdot \frac{\partial x_\nu}{\partial x'_\gamma} \,.\, A_{\mu\nu}, \quad . \quad . \quad . \quad . \quad . \quad (2\cdot3)$$

while if α and β are different,

$$A'_{\alpha\beta} - \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \,.\, A_{\mu\nu} + A'_{\beta\alpha} - \frac{\partial x_\mu}{\partial x'_\beta} \cdot \frac{\partial x_\nu}{\partial x'_\alpha} \,.\, A_{\mu\nu} = 0. \quad (2\cdot4)$$

The last term in (2·4) can be written

$$-\frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \,.\, A_{\nu\mu},$$

so that (2·4) can be written

$$A'_{\alpha\beta} + A'_{\beta\alpha} = \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} (A_{\mu\nu} + A_{\nu\mu}). \quad . \quad . \quad (2\cdot5)$$

If now we write

$$\tfrac{1}{2}(A_{\mu\nu} + A_{\nu\mu}) = B_{\mu\nu} = B_{\nu\mu}$$

and
$$\tfrac{1}{2}(A'_{\alpha\beta} + A'_{\beta\alpha}) = B'_{\alpha\beta} = B'_{\beta\alpha},$$

then
$$B'_{\alpha\beta} = \frac{\partial x_\mu}{\partial x'_\alpha} \cdot \frac{\partial x_\nu}{\partial x'_\beta} \,.\, B_{\mu\nu}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\cdot6)$$

so that $B_{\mu\nu}$ is a tensor.

If the A's are symmetrical so that $A_{\alpha\beta} = A_{\beta\alpha}$, then $B_{\alpha\beta} = A_{\alpha\beta}$, and $A_{\mu\nu}$ is a tensor.

For example, the invariance of $g_{\mu\nu} \,.\, dx_\mu \,.\, dx_\nu$ *combined with the symmetry of* $g_{\mu\nu}$ establishes the fact that $g_{\mu\nu}$ is a tensor.

On the other hand, we may write

$$ds^2=(g_{\mu\nu}+F_{\mu\nu})dx_\mu \,.\, dx_\nu,$$

where $F_{\mu\nu}$ is any antisymmetrical function of μ and ν, without altering the value of ds^2; and it does not follow that $g_{\mu\nu}+F_{\mu\nu}$ is a tensor.

In Eddington, § 29, it is shown that

$$\frac{dx}{ds}\cdot\frac{dx_\nu}{ds}\left(\frac{\partial A_\mu}{\partial x_\nu}-\{\mu\nu,\alpha\}A_\alpha\right) \text{ is invariant};$$

we cannot infer that the quantity in brackets is a tensor but only that

$$\frac{1}{2}\left(\frac{\partial A_\mu}{\partial x_\nu}+\frac{\partial A_\nu}{\partial x_\mu}\right)-\{\mu\nu,\alpha\}A_\alpha \text{ is a tensor.}$$

§ 5. Similar results hold for higher tensors.

Thus, if in a 3-dimensional system the quantity

$$A_{\mu\nu\sigma}\,.\,dx_\mu\,.\,dx_\nu\,.\,dx_\sigma$$

is invariant, we cannot infer that $A_{\mu\nu\sigma}$ is a tensor.

On the other hand, $B_{\mu\nu\sigma}$ is a tensor where

$$\begin{aligned}
&B_{aaa}=A_{aaa}\\
&B_{aab}=B_{aba}=B_{baa}=\tfrac{1}{3}(A_{aab}+A_{aba}+A_{baa})\\
&B_{abc}=B_{acb}=B_{bac}=B_{bca}=B_{cab}=B_{cba}\\
&=\tfrac{1}{6}(A_{abc}+A_{acb}+A_{bac}+A_{bca}+A_{cab}+A_{cba}),
\end{aligned}$$

the twenty-seven elements of the tensor being represented by only ten distinct quantities.

[This limitation of the quotient law is mentioned in the *second* edition of my 'Mathematical Theory of Relativity' (Note 2, p. 242), which Prof. Brown will not have seen; but the point is of much importance, and I welcome his discussion of it. For the sake of clearness it should be pointed out that in my enunciation of the rigorous quotient theorem the multiplier is a *vector*, not a general tensor as in Brown's enunciation; and that his remarks refer in most cases to what I have called the argument from covariant dimensions which is not claimed to be rigorous. That does not in any way diminish their value and instructiveness. In general I did not trouble about rigour in the deduction of the various tensors, since the main point was the method of discovery of the expressions; once found, their tensor character could be tested in other ways, but any proof that $g_{\mu\nu}$ is a tensor professed to be rigorous, and in this case I fell into the trap similar to the one which Prof. Brown here exposes.—A. S. EDDINGTON.]

LXVIII. *A Method for Exciting Spectra of Certain Metals.*

By JOHN K. ROBERTSON, *Associate Professor of Physics, Queen's University, Kingston, Canada*.*

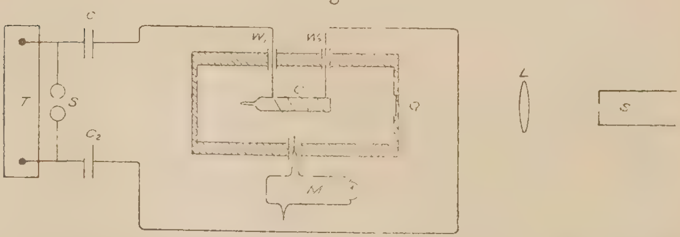
[Plate XII.]

Introduction.

A YEAR or more ago, in order to obtain information which might prove of value in analysing the spark spectrum of tin, an attempt was made to excite the vapour of that element by the use of the electrodeless discharge. Because of residual gas which developed at the high temperature at which it was necessary to work, the attempt was only partially successful. A control spectrum of the discharge carried by the residual gas in the tube at room temperature, however, revealed an interesting result. *Characteristic tin lines were present in this spectrum almost to the same extent as in those obtained with the tube at a temperature in the neighbourhood of* 1000° *C.* As the vapour pressure of tin under conditions of the control spectrum could not have exceeded 10^{-20} mm., the origin of the metallic lines in this case was somewhat puzzling, and it seemed worth while to see if the same effect could be obtained with other metals. This was done with zinc, cadmium, silver, and gold with results which, together with a discussion of the possible cause of the appearance of the lines, are reported in the present paper.

Experimental.

Fig. 1.



To obtain an electrodeless discharge in tin vapour, it was obvious at the outset that temperatures at least as high as 1000° C. would be necessary. For that purpose a cylindrically shaped oven was constructed with a quartz window Q at the centre of one end, and with inlets for the insertion of one junction of a thermocouple M and for the high-frequency leads

* Communicated by the Author.

W_1 and W_2. These leads were the ends of a cylindrical coil C of heavy nickel wire, consisting of 12 turns tightly wrapped around an alundum tube supported along the horizontal central axis of the oven. To obtain high-frequency currents, leyden jars C_1 and C_2 were charged by means of a small interrupterless X-ray transformer T, while the intensity of discharge in the oscillatory circuit containing the condensers and the coil C was controlled by means of the spark-gap S. Frequencies of the order of 10^8 per second were used. A highly exhausted cylindrical quartz tube, 3·2 cm. in diameter, 15 cm. long, containing pure tin, was placed within the alundum tube and exciting coil. As the quartz tube had previously been subjected to a careful preliminary outgassing and heating, it was hoped that a pure tin discharge would be obtained when the sealed-off tube was heated to 1000° C. To examine the spectrum of any such discharge light from the quartz tube was focussed, by means of the quartz lens L, on the slit of a small Hilger spectrograph S.

With the first tube discharges were obtained and spectrograms taken at temperatures ranging from 700° C. to 1000° C., in some cases with different degrees of excitation. It was evident, however, that at least part of the discharge was carried by residual gas. This may readily be seen by an examination of a typical spectrogram shown in Plate XII. (fig. 2 *a*), in which, in addition to the prominent arc and a few spark lines of tin, some due to gas and to other impurities are present. Attention may also be directed to the fact that, in spite of the use of liquid air and phosphorus pentoxide, the characteristic water-vapour band with head at 3064 is strongly developed.

The tube was now re-opened, attached to the evacuating system, washed out, when hot, with hydrogen to reduce possible oxides, and finally subjected to further heating and outgassing in the hope of removing all traces of residual gas and water vapour. On sealing off from the pumps the tube was once more placed in the oven and photographs taken of the spectrum of the discharge obtained at 900° C. or higher. In Plate XII. (fig. 2 *b*) the result is shown. Residual gas and water vapour are still present, while, in spite of the use of liquid air, a few mercury lines have made their appearance. It is significant that tin lines are considerably less prominent in this spectrum than in fig. 2 *a*, where mercury lines are absent.

In view of the failure to remove completely residual gas and water vapour, it was next decided to see if, with a new tube, a pure tin discharge could not be obtained with the tube

attached to the evacuating system while at the same time it was heated in the oven to 1000° C. Under these conditions absolutely no discharge was obtained, although a deposit of tin gradually became visible on the walls of a portion of the connecting tube outside the oven. At this temperature a vapour pressure sufficiently high to permit of a discharge could not be obtained—at any rate, maintained—inside the tube. This tube was now subjected to a very drastic heating and outgassing, and once more an attempt was made to obtain a pure tin discharge when the sealed tube was used.

This time somewhat better success was attained, as initially a continuous discharge was not obtained until a temperature in the neighbourhood of 900° C. was reached, an indication that residual gas was not present to any marked degree. The discharge then obtained was characterized by a general glow, of slightly bluish cast which deepened as the temperature rose slightly. Its spectrum revealed a continuous region extending from 2000 Å.U. almost to the visible region, together with tin arc lines superimposed and certain impurities. At 1000° C. the characteristic white *ring* discharge developed, as will be evident from the increased intensity at the outer edges of the spectrogram in Plate XII. (fig. 3 *a*). It will be noticed that the water-vapour band is again present. Unfortunately, while the exposure for this plate was in progress, a short-circuiting of one of the heating coils in the oven caused a rise in temperature higher than any which had hitherto developed and the discharge disappeared. This was doubtless due to the development of a gas pressure above that at which an electrodeless discharge could be obtained, for on cooling the tube, a bright discharge could be obtained at room temperature without difficulty. A control spectrum taken with the tube "cold," and shown in Plate XII. (fig. 3 *c*), revealed an interesting result. As is clearly shown in the reproduction, *almost all the strong lines below* 3000 *are due to tin, and, with few exceptions, characteristic tin lines are present in this spectrum to the same extent as in fig.* 3 *a*, *that taken at* 1000° *C.* This result was corroborated by examination of a spectrogram taken, purely for purposes of alignment, when the attempt was made to obtain a tin discharge with the tube attached to the pumping system. In this case, air at a pressure of the order of 1/10 mm. had been left in the apparatus to carry the discharge, while the tube contained metallic tin. In Plate XII. (fig. 3 *b*) the spectrum obtained under such conditions has been placed alongside those corresponding to the "cold" and the 1000° C. discharges, and again it will be noticed that in fig. 3 *b* tin

lines have come out much as in the other two. As an ordinary dry plate was used to obtain this spectrogram, and Schumann plates for 3 *a* and 3 *c*, the effect is not so striking.

At this stage, therefore, the writer was interested in two questions: (1) Where did the water vapour come from? (2) What was the origin of the tin lines occurring at temperatures corresponding to which the vapour pressure is extremely low?

A visit to the Research Laboratory of the General Electric Company, Schenectady, N.Y., supplied the answer to the first question. The experience of workers in that laboratory has shown that water vapour is given off from hot quartz and that it is a very difficult matter to get rid of it. In spite of careful outgassing, therefore, in the experimental conditions described above, the presence of the water-vapour band is not surprising.

To provide additional information which would probably help to answer the second question, it was obviously desirable to see if the same effect could be obtained with other metals. This was done with cadmium, zinc, silver, gold, and again with tin to verify earlier work. In all subsequent work the quartz tube was attached to the evacuating system and sufficient gas was left in the apparatus to carry the discharge. As hydrogen lines had been prominent in the early work, for the most part this gas, at a pressure of 1/10 mm. or less, was used and spectrograms were made with a U-tube immersed in liquid air to keep mercury vapour out of the quartz tube.

Cadmium.

In the case of cadmium, Plate XII. (fig. 4) shows the

Table II.

Wave-length.	Series Notation.	
2144	$1\sigma-1\pi_1$	Cd+
2265	$1\sigma-1\pi_2$	Cd+
2288	1S−1P	Cd
3261	$1S-1p_2$	Cd

result obtained with the quartz spectrograph. Only the few lines given in Table II. came out with marked intensity.

Other lines were entirely absent, with the exception of one or two whose intensity was many times less than that of those given in the table. Another spectrogram taken with a glass prism spectrograph in the visible region showed the triplet 5086, 4800, 4678 ($1p-1s$) strongly developed, and a line which is possibly 4413 ($1p_2-2S$).

It will be evident, therefore, that the only lines which appear with considerable intensity are ultimate and penultimate lines of the neutral atom, together with ultimate lines of the ionized element *. The significance of this will be discussed later.

Zinc.

In the case of zinc similar results were obtained. The few lines which stood out prominently in the ultra-violet, as shown in Plate XII. (fig. 5) and in Table III., are again ultimate or penultimate lines of the neutral, together with two ultimate of the ionized atom. As the quartz tube used for this metal had been previously used for cadmium, in spite of careful cleaning a few cadmium lines are present.

TABLE III.

Wave-length.	Series Notation.	
2025	$1\sigma-1\pi_1$	Zn+
2062	$1\sigma-1\pi_2$	Zn+
2133	$1S-1P$	Zn
3302	$1p_1-2d$	Zn
3345	$1p_2-2d$	Zn

In repeating observations with tin under similar conditions, it was shown not only that the characteristic lines came out to much the same extent as in earlier work, but also that it was not necessary to have a deposit of metal on the tube. There was little difference in two spectrograms taken, one before fresh pieces of tin had been subjected to any heating, the other after an oxygen-gas flame had been played on the tube until a visible deposit had formed on the walls of the tube.

* For explanation of these terms see Russell, Astrophys. J. iv. p. 223 (1925).

Mercury.

Attention has already been directed to the fact that in Plate XII. (fig. 2 *b*) a few mercury lines are evident. An examination of these shows the presence, with considerable intensity, of two lines usually assigned to the ionized atom, together with ultimate and penultimate neutral lines, the strongest of which below 3000 are shown in Table IV.

TABLE IV.

Wave-length.	Series Notation.		Intensity.
2224·8	?	Hg+	Strong.
2536·5	$1S-1p_2$	Hg	,,
2847·8	?	Hg+	,,
2967·3	$1p_3-2d$	Hg	,,
2652±	$1p_2-3d$	Hg	Weak.
2893·6	$1p_2-2s$	Hg	,,

Silver and Gold.

With these metals negative results were obtained, although it should be stated that in the case of silver, the lines to be expected, 3383 and 3280, are in the region of small dispersion where it is difficult to identify lines with certainty.

To sum up, then, it has been shown that, by allowing a gas to carry an electrodeless discharge in a tube in which a metal has been placed, spectral lines characteristic of the metal are brought out in the case of tin, cadmium, and zinc. Moreover, the zinc and cadmium lines, which are few in number, are fundamental, both as regards the neutral and the ionized atom.

Discussion.

In seeking for the origin of these metallic lines, two possible causes suggest themselves: (1) The effect is simply one of vaporization, as a result of which sufficient atoms are present in the discharge region to give rise to lines of marked intensity. (2) The atoms of the metal are present as a result of a reaction, chemical or otherwise, between excited gas atoms and the metal or an oxide of the metal. We shall first of all examine the evidence for and against the vaporization theory.

Although the discharge begins at room temperature, there is considerable energy absorbed and after an exposure of ten or fifteen minutes the exciting coil as well as the quartz tube are decidedly warm. A piece of metal or thin metallic layer, therefore, would rise in temperature considerably. To obtain some idea of the magnitude of such a rise, a Brown thermocouple was placed within the exciting coil, (*a*) within a thin copper shield, (*b*) without the copper shield. In the second case, after 15 minutes there was a rise in temperature to 100° C. without any sign of a maximum, while, with the shield, after 10 minutes a temperature of 125°, approaching a maximum, had been recorded. There seems no doubt, therefore, that the metal would become hot. On the other hand, pieces of tin (melting-point = 232° C.) did not melt, so that we may reasonably assume 200° C. as an upper limit to the possible temperature attained during the time of exposure. In some cases this was less than 10 minutes.

TABLE V.

Metal.	100° C.	200° C.
Cd	4×10^{-5} mm.	2×10^{-3} mm.
Zn	3×10^{-6} ,,	9×10^{-4} ,,
Sn	4×10^{-24} ,,	9×10^{-18} ,,
Au	$5{\cdot}5\times10^{-26}$,,	5×10^{-20} ,,
Ag	4×10^{-18} ,,	1×10^{-13} ,,

In Table V. approximate vapour pressures of cadmium, zinc, tin, gold, and silver have been given at temperatures of 100° C. and 200° C. A glance at this table will show that in the case of cadmium and zinc, undoubtedly ordinary vaporization may be responsible for the effect observed. In this connexion it should be stated that a visible cadmium deposit was formed in the tube, but none with zinc. In the case of tin, however, we can reasonably conclude that the vapour pressure could not possibly exceed 10^{-20} mm. Can we detect spectral lines with such a low pressure? That is a question which experiment alone can answer, and the writer has under way an investigation designed to throw light on the matter. In the meantime it seems extremely unlikely that lines as strong as those shown in Plate XII. (fig. 3 *c*), for

example, could come out with a vapour density as low as that corresponding to such a pressure. It is doubtful, therefore, if ordinary vaporization due to rise in temperature can be the cause in the case of tin, and it does not necessarily follow that it must be so even for cadmium and zinc. Confirmation of the probable correctness of this conclusion is found in the work of Goldstein* on the appearance of metallic lines in the discharge of a vacuum tube containing nitrogen. Not only were lines characteristic of the metallic cathode present, but they appeared with increased intensity when the vacuum-tube was immersed in liquid air.

The spectroscopic information obtained by the writer is not without its significance. In the case of zinc, cadmium, and mercury it has already been emphasized that ultimate lines of the ionized atom were present, while higher members of the ordinary arc series were either absent or of feeble intensity. This result is somewhat surprising. Why should ultimate lines of the ionized atom appear with marked intensity, while higher members of arc series, which require less excitation, are absent altogether? If metallic atoms were in the discharge region as a result of ordinary vaporization, it is difficult to see why this should be the case. Undoubtedly with hydrogen carrying the discharge, there would be many electrons present with sufficient velocity to ionize these metallic atoms, and the resulting ions could easily be excited to radiation. At the same time, however, higher members of neutral series should come out. This is all the more to be expected when the pressure of the vapour is a small fraction of the total, for, in that case, the "expectation of life" of the neutral atom is increased.

In this connexion reference may be made to the somewhat related work of Merton and Pilley † on nitrogen and Paschen ‡ on aluminium. The former investigators showed that when a feebly condensed discharge took place in helium (at 30 mm. pressure) which contained an "extremely small amount" of nitrogen, a true arc spectrum of this gas was obtained "completely isolated from the spark." Conditions, however, were by no means identical with those we are discussing, for comparatively few electrons sufficient to ionize nitrogen atoms were present.

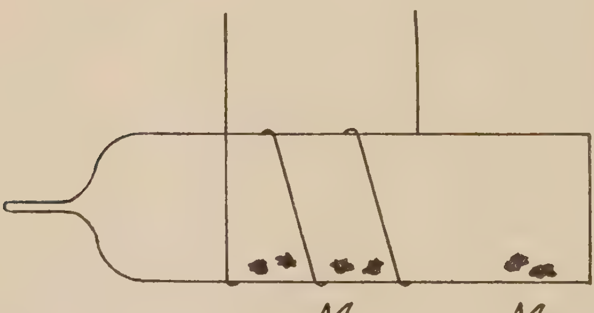
Paschen, using a discharge in a vacuum-tube, with a cylindrical cathode of aluminium containing pure helium,

* Goldstein, *Phys. Zeitschr.* vi. p. 14 (1905).
† Merton and Pilley, Proc. Roy. Soc. A, cvii. p. 411 (1925).
‡ Paschen, *Ann. d. Phys.* lxxi. p. 142 (1923).

found that lines of neutral and singly ionized atoms (Al I and II) came out, whereas in the ordinary spark lines of Al I, II, and III were present. Moreover, higher members of Al II were present in the case where a trace of the vapour was present in the discharge than in the Al II of the ordinary spark. It seems remarkable, therefore, that in the case of the electrodeless excitation higher members of arc series should be absent and ultimate ionized lines present.

Something may be said in favour of the other possible explanation, that metallic ions find themselves in the discharge region as a result of some kind of reaction between active gas atoms or gas ions and the metal or an oxide of the metal. In the first place, pieces of metal lying in the high-frequency field are undoubtedly in a favourable state for such a reaction. Evidence of this is found in the work of Bloch and Bloch * on sodium chloride. These investigators have found that when a high vacuum has been attained in a tube containing this salt, an electrodeless discharge takes place with

Fig. 6.



chlorine lines very prominent. Moreover, once the excitation is removed, it is necessary to re-admit air in the apparatus and to re-exhaust before the "chlorine" discharge can again be obtained. In the present investigation it was observed that pieces of zinc placed directly within the exciting field, as at M_1, fig. 6, had completely lost the whitish-grey coating usually to be found on that metal, whereas other pieces outside the field, as at M_2, remained in the original condition. It looks, therefore, as if a kind of cleaning up process was at work, and it is not improbable that a reduction of an oxide took place, zinc *ions* being liberated in the process.

* Bloch and Bloch, *Compt. Rend.* clxxx. p. 1740 (1925).

As in the case of tin, air was as effective as hydrogen in bringing out metallic lines, the oxide theory is not altogether satisfactory. It may be that the metal is put in a favourable state so that metal ions are pulled off, as it were, as a result of bombardment by the gaseous ions carrying the discharge. Some work of Langmuir shows that, under certain conditions, metallic coatings on walls may be removed by such means. Regarding this point additional information might be obtained by the use of an inactive residual gas such as helium, and, in the near future, the writer hopes to make such a test.

If metallic *ions*, not neutral atoms, find themselves in the discharge region because of some such reaction, then a possible explanation of the appearance of ultimate ionized lines, and non-appearance of higher members of neutral series, may be suggested. Some of these ions would be excited to radiation, possibly as a result of collisions of the second kind, while many neutral atoms would be formed by re-combination. Such atoms would subsequently be excited, but because of the excess of low-voltage electrons, which it is not improbable to assume exists in the alternating electrodeless field, ultimate and penultimate lines would greatly exceed in intensity higher members of neutral series. The same explanation might reasonably be applied to mercury, for the presence of this vapour (in fig. 2 *b*) may have been the result of the formation of an oxide of that element when the hot tube was being washed out with hydrogen.

Whatever the explanation of the effect, the result should be of value in spectroscopic analysis. Any method which throws into relief fundamental spectral lines is valuable, and the writer hopes to put this one to use, not only in work on the spectrum of tin but in the case of other metals.

The writer has pleasure in acknowledging his indebtedness to the Research Council of Canada for a grant which enabled him to purchase quartz apparatus ; to Mr. J. T. Thwaites, B.Sc., for assistance in constructing the electric oven, and to the Electrical Alloy Company of Morristown, N.J., for the gift of a coil of heavy nickel wire.

Department of Physics,
Queen's University,
Kingston, Canada,
November, 1925.

LXIX. *The Evacuation of Carbon Dioxide and Water.* By N. R. CAMPBELL. (Communication from the Staff of the Research Laboratories of the General Electric Co., Wembley)*.

SUMMARY.

WHEN a cooled trap is used for removing mercury vapour, there is a danger that substances may condense in the trap and establish in the vessel to be evacuated a pressure, large enough to be appreciable, yet small enough to prevent the rapid removal of the substance by the pump. If the trap is cooled in liquid oxygen boiling at atmospheric pressure, carbon dioxide condenses in this manner; if solid CO_2 is used, water condenses. Accordingly if these substances are present and a pressure is to be obtained as low as that possible in their absence, the trap must be maintained at some other temperature. It can easily be maintained (1) at 78° K. by boiling the oxygen under reduced pressure or (2) between 108° and 150° K. by means of solid mercury cooled by liquid oxygen. At either of these temperatures, pressures less than 10^{-7} mm. can be obtained quickly, even if water and carbon dioxide are present. The vapour pressure of CO_2 at 90°·2 K. is a convenient standard for calibrating ionization gauges.

WHEN a cooled trap to absorb mercury vapour is placed in a pumping circuit, the evacuation involves two distinct processes. Gases such as oxygen are removed by pumping, mercury vapour by condensation at a temperature at which its vapour pressure is inappreciable. It does not seem always to be realized that this combination of two processes may lead to the failure of both. If there is present in the system a substance of which the vapour pressure at the temperature of the trap is of the order of 10^{-5} mm., its vapour pressure will be appreciable and greater than that easily attained by the pump, and yet it will be so low that the substance will be pumped away extremely slowly. It will be "condensed" in the trap, but it will establish on the far side of it a constant pressure which will be independent of the action of the pump and will not fall until the whole of the substance has been removed. If the pressure is 10^{-5} mm. and the effective volumetric speed of the pump 1 litre per second, the removal of gas occupying 1 c.c. at N.T.P. will require 21 hours.

The temperatures at which such a trap are most often

* Communicated by the Director.

maintained are 194°·9 K. (solid CO_2) and 90°·2 K. (liquid oxygen). The "condensible" gases (other than mercury) most likely to be present in a pumping system are water and carbon dioxide. It is unfortunate that at the higher temperature water, and at the lower carbon dioxide, has a vapour pressure within or near the dangerous range. The vapour pressure of water (ice) at temperatures above 200° K. has been measured by Scheel and Hause *; we have discovered no measurements at lower temperatures, but by extrapolating their formula

$$\log_{10} p(\text{mm.}) = 11{\cdot}50406 - 0{\cdot}4 \log_{10}\mathrm{T} - \frac{2694{\cdot}2}{\mathrm{T}},$$

we find

$$p = 3{\cdot}67 \times 10^{-4} \quad \text{at} \quad 194^\circ{\cdot}9 \text{ K.}$$

The vapour pressure of carbon dioxide has been measured down to 90° K. by Onnes and Weber †, their formula

$$\log_{10} p(\text{mm.}) = -\frac{1314{\cdot}35}{\mathrm{T}} + 1{\cdot}75 \log_{10}\mathrm{T} - 0{\cdot}0019707\mathrm{T} + 6{\cdot}0508$$

gives

$$p = 5{\cdot}29 \times 10^{-6} \quad \text{at} \quad 90^\circ{\cdot}2 \text{ K.}$$

A correction to these values, due to Knudsen ‡, has to be applied in order to obtain the pressure which will be established in a vessel at room temperature connected to the trap. If p, T are the pressure and temperature in the trap, p', T′, in the vessel at room temperature,

$$\frac{p}{p'} = \sqrt{\frac{\mathrm{T}}{\mathrm{T}'}}.$$

The correcting factor at 194°·9 K. is 1·22, at 90·2° K. 1·79.

With a trap cooled in liquid oxygen it is not difficult to reach a pressure of 10^{-6} mm. in a vessel which can be baked during exhaustion; the danger from carbon dioxide cannot therefore be as great as might have been anticipated. The limit of pressure easily obtainable with solid carbon dioxide is less well known, but it has been thought worth while to make a few rough measurements in order to ascertain more precisely what the effect of the presence of these substances is likely to be in an actual pumping system.

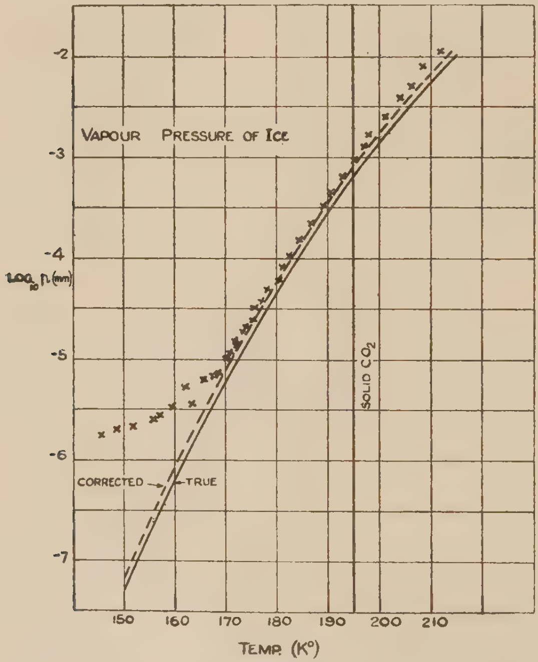
* K. Scheel and W. Hause, *Ann. d. Phys.* xxix. p. 723 (1909).

† H. K. Onnes and S. Weber, *Kon. Akad. Weten. Amst. Proc.* xvi. p. 445 (1913).

‡ M. Knudsen, *Ann. d. Phys.* xxxi. p. 205 (1910).

For this purpose an ionization gauge was pumped in the ordinary way through a cooled trap into which water or carbon dioxide could be admitted in known quantities. The filament of the gauge decomposes both these substances, and therefore alters the pressure when they are present; but since the pressure did not alter rapidly when the filament was heated, this source of error was immaterial for the present purpose. The gauge was calibrated against a McLeod gauge when filled with nitrogen, and Dushman's rule was used to apply this calibration to other substances.

Fig. 1.

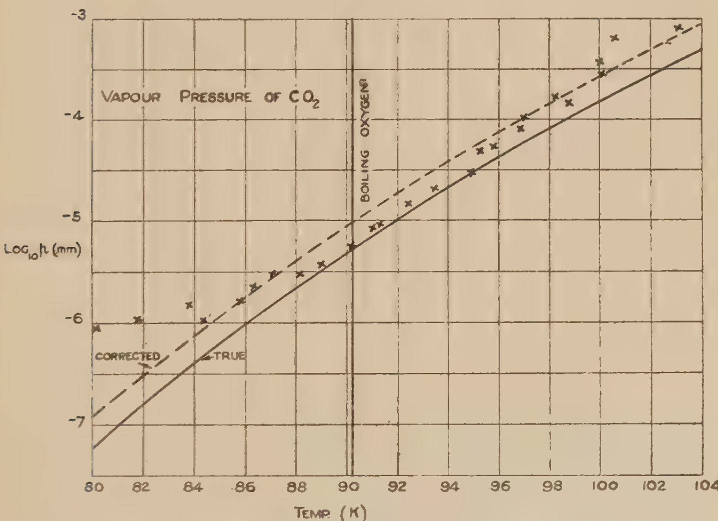


For temperatures above 90° K., the trap was frozen in mercury in a Dewar flask by means of liquid oxygen, and the temperature allowed to rise naturally at the rate of about 10° an hour; for temperatures below 90°, the trap was immersed in liquid oxygen boiled at reduced pressure. The temperature was measured by a thermocouple.

The results of these measurements are shown in figs. 1 and 2, the points of which show the logarithm of the pressure in the gauge at various temperatures of the trap

into which carbon dioxide or water has been introduced. The full lines are the curves of Onnes and Weber and of Scheel and Hause, the dotted lines the corresponding values when Knudsen's correction is applied. At the higher pressures the divergence of the points from the dotted curve is not greater than can be accounted for by uncertainties in the calibration of the gauge and of the thermocouple; it is clear that the pressure in the gauge is determined, as it should be, by the vapour pressure of the condensed substance. But at the lowest temperatures,

Fig. 2.



the pressure in the gauge tends to a constant value much greater than the vapour pressure; there is a limit to the vacuum which can be reached independent of the substance condensed in the trap.

The existence of such a limit is, of course, characteristic of all evacuating systems; it is generally associated with gas present on the surfaces within the gauge or on the tubes connecting it with the pump; if suitable measures had been taken, the limit could doubtless have been considerably reduced. But the point important for our purpose is that, without any such measures, the limit is only about 1/10 of the pressure due to carbon dioxide in a trap at 90°·2 and only about 1/500 of that due to water in a trap at 194°·9; if traps at these temperatures

are used, these substances must be completely removed if they are not to set the limit to the pressure attainable. On the other hand, water need not be removed if liquid oxygen is used; and, if the trap is cooled to 78° K. (either by boiling the oxygen under reduced pressure or by using liquid nitrogen), the presence of carbon dioxide would not be harmful even if the pressure attainable in its absence was as low as 10^{-7} mm.

There is another alternative conceivable: there may be a temperature above 90° at which the vapour pressure of carbon dioxide is so high that it is pumped away as quickly as a permanent gas, while that of water is so low that it is inappreciable. To discover whether there is such a temperature some observations were made on the time necessary to remove by pumping a known quantity of carbon dioxide introduced into the trap maintained at a known temperature. The results varied greatly, and in apparently similar experiments times in the ratio of 3 to 1 were obtained; probably the time depends on the distribution of the substance in the trap. If S is the volumetric speed of the pump, p the vapour pressure at temperature T, the time t required to remove a quantity of substance which would occupy a volume V at pressure p and temperature T should be given by

$$t=\frac{V}{S}.$$

If the time to remove the substance is identified with that required to make the pressure in the gauge begin to fall rapidly, it is of the same order as that calculated. On the other hand, the time to remove the substance completely, and to reach again the limiting pressure obtaining before the substance was introduced, is very much greater; for the initial rapid decrease corresponding to the volumetric speed is not maintained. The explanation is doubtless that some of the substance is absorbed on the glass and in that state possesses an effective vapour pressure very much less than that of the main portion. The amount of the gas so absorbed increases with the time that the glass is exposed to the gas; the practical question of importance is how high must the temperature of the trap be in order that a substance, admitted to it while the pump is acting, will be pumped away so quickly that it has no time to be absorbed and will therefore produce no permanent increase in the limiting pressure.

This question can be answered definitely only for an actual

piece of apparatus. The volume of our apparatus up to the cut-off was about 800 c.c.; the effective volumetric speed was 120 c.c. per sec. The admission to the trap of 0·1 c.c. of carbon dioxide or water (measured at N.T.P.) did not cause any permanent increase if the temperature of the trap was so high that the vapour pressure of the substance was at least 0·005 mm.; but if the vapour pressure was as low as 0·0005 mm., or, if 1 c.c. of the substance was admitted, some permanent increase was caused. Figs. 1 and 2 show that in the interval 108° K. and 150° K. the vapour pressure of carbon dioxide is above 0·005 mm. and that of water below 10^{-7} mm. Consequently if the trap is kept at some temperature in this range, carbon dioxide will be removed as a permanent gas and water completely condensed; neither will exert a permanent pressure.

When carbon dioxide is likely to be present (water can hardly ever be avoided) and pressures of 10^{-6} mm. have to be attained, there are then two alternatives. One is to use a colder trap; the other to use a warmer. Our experiments do not indicate that there is any ground for preferring one to the other, except in respect of ease of maintaining the necessary temperatures. In neither case are the difficulties serious. For the lower temperature liquid nitrogen can be used, but it is more expensive than liquid oxygen; an easier plan is to boil the oxygen at reduced pressure. All that is necessary for this purpose is to pass the trap into the Dewar flask through a rubber bung and to connect the interior to any rough vacuum. The evaporation of the liquid is not markedly more rapid than when the pressure is atmospheric. It is not even necessary to maintain continuously the connexion to the vacuum. When the pressure rises again to atmospheric, the liquid oxygen begins to boil at the surface, but unless the liquid is stirred vigorously, the lower layers will remain for a long time at the temperature to which they have been reduced by boiling at the reduced pressure. In a reasonably good Dewar flask, the temperature may be maintained at 80° K. by connecting the flask to the vacuum for a minute every half hour.

For the higher temperature there is no convenient constant temperature bath; but, since the range of temperature permissible is wide, none is needed. It is sufficient to fill a flask half full with mercury (interposing a layer of paper between the metal and the glass to reduce the chance of fracture) and to cool it by liquid oxygen poured

on the surface until the temperature, indicated by a copper-constantan couple connected to a pointer galvanometer, is within the desired range. To keep it within that range a little more oxygen has to be added every two or three hours.

It may be pointed out incidentally that the vapour pressure of carbon dioxide at 90°·2 is a convenient rough standard for the calibration of ionization gauges, account being taken of the Knudsen correction.

LXX. *On the Quantitative Theory of Induction Heating.*

By C. R. Burch, *B.A.*, *and* N. Ryland Davis, *B.A.**

Summary.

This paper investigates the energetics of an induction furnace, and discusses the conditions under which the transfer of energy from inductor to charge is maximal, and the influence of the various operating parameters on the "power factor" of the loaded inductor.

Introduction.

An induction furnace—an apparatus in which conducting bodies may be heated by the eddy-currents produced in them under the influence of an alternating magnetic field —is already an indispensable piece of laboratory equipment, and is finding an ever-increasing application in commercial practice. Since Dr. Northrup's † paper, much has been written on the practical side of the subject, and formulæ have been developed determining the performance of an induction furnace; some of these are not too reliable.

The object of this paper is to develop a theory of the subject founded on sound physical reasoning, and some attempt at mathematical rigidity.

To crystallize our ideas, let us consider a thin annular charge, inductance L, resistance R, in an inductor L′, R′, in which current (equal to the real part of $I\epsilon^{ipt}$) flows.

The current in the charge will then be denoted by the complex $\frac{ipM}{R+ipL}I\epsilon^{ipt}$, where M is the mutual inductance between the charge and inductor.

* Communicated by Prof. C. G. Darwin, F.R.S.

† E. F. Northrup, Trans. Am. Electrochem. Soc. vol. xxxv. (1919).

The rate of generation of heat in the inductor will be $\frac{1}{2}R'|I|^2$, and that in the charge, $\frac{p^2M^2R|I|^2}{2(R^2+p^2L^2)}$, where M is the inductor and charge.

The fraction of the total power supplied to the inductor, which appears as heat in the charge, will be called the "efficiency" of the inductor, and will be denoted by η.

It is
$$p^2M^2R/[p^2M^2R+R'(R^2+p^2L^2)].$$

We want η to be high, and it is a maximum if p is infinite. (L, R, L′, R′ are supposed independent of p.)

It behoves us to examine whether this frequency has any more obscure disadvantages. As regards the generator, its losses are proportional to the product of the R.M.S. current and R.M.S. voltage at its terminals, and in our simple case are proportional to the frequency, when this is high. We can annihilate the reactance of the inductor at a given frequency by placing in parallel with it a condenser of capacity given by

$$C = L_0/[R_0{}^2+p^2L_0{}^2],$$

where

$$R_0 = R'+\frac{p^2M^2R}{R^2+p^2L^2} \quad \text{and} \quad L_0 = L'-\frac{p^2M^2L}{R^2+p^2L^2}$$

are the effective resistance and reactance of the loaded inductor. The generator need then only supply that part of the inductor current which is in phase with its voltage, the condenser supplying the power necessary to vary the energy stored magnetically by the system. This power, which is necessary to overcome the effective reactance of the inductor, is dynamically conserved, and its R.M.S. value will be termed "conserved power." The losses in the condenser (ohmic and hysteretic), though far smaller than the corresponding losses, in its absence, in the generator, are in practice appreciable, being proportional to the power which it conserves. Condensers capable of conserving high powers are exceedingly expensive; it may therefore be (and in general is) as important to obtain a low ratio of "conserved power" to charge heating as it is to obtain the highest possible ratio of charge heating to inductor loss. We can conveniently calculate the "conserved power" by the following method.

If the inductor voltage is represented by the real part of $V' = V\epsilon^{ipt}$, we can write

$$V' = |V|\epsilon^{i(pt+\gamma)}, \quad . \quad . \quad . \quad . \quad . \quad \text{(defining } \gamma\text{)}$$

$$I' = I\epsilon^{ipt} = |V| . \left[\frac{R_0-ipL_0}{R_0{}^2+p^2L_0{}^2}\right]\epsilon^{i(pt+\gamma)}.$$

Now take

$$\tilde{\mathrm{V}}' = |\mathrm{V}|\, \epsilon^{-i(pt+\gamma)},$$

and form the complex product

$$\tfrac{1}{2}\tilde{\mathrm{V}}'\mathrm{I}' = \tfrac{1}{2}\left[\frac{\mathrm{R}_0 - ip\mathrm{L}_0}{\mathrm{R}_0^2 + p^2\mathrm{L}_0^2}\right] . |\mathrm{V}|^2.$$

This is independent of γ and t, and therefore

$$\tilde{\mathrm{V}}'\mathrm{I}' = \tilde{\mathrm{V}}\mathrm{I}.$$

Its real part is equal to the dissipated power, while its imaginary part determines the "conserved power." A sign convention is necessary, and we shall say

$$\left.\begin{aligned} \mathrm{P}_d &= \text{real part of } \tfrac{1}{2}\tilde{\mathrm{V}}\mathrm{I}, \\ \mathrm{P}_c &= \quad ,, \qquad ,, \quad ,, \quad \tfrac{1}{2}i\tilde{\mathrm{V}}\mathrm{I}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1)$$

That is to say, we shall consider the power conserved by an inductance as positive.

We can extend (1) to the case of a radially thick inductor and solid charge, as an integral:

$$\left.\begin{aligned} \mathrm{P}_d &= \text{real part of } \tfrac{1}{2}\int_{r_1}^{r_2} \tilde{\mathrm{V}}_r j_r\, dr, \\ \mathrm{P}_c &= \quad ,, \qquad ,, \quad ,, \quad \tfrac{1}{2}i\int_{r_1}^{r_2} v_r j_r\, dr, \end{aligned}\right\} \quad . \quad . \quad . \quad (2)$$

where v_r and the current density j_r may both depend on the radius.

We shall use (2) to define the effective resistance and reactance of the system in the following way:

$$\left.\begin{aligned} \tfrac{1}{2}|\mathrm{I}|^2\mathrm{R}_0 &= \mathrm{P}_d, \\ \tfrac{1}{2}|\mathrm{I}|^2 p\mathrm{L}_0 &= \mathrm{P}_c. \quad \left(\mathrm{I} = \int_{r_1}^{r_2} j_r\, dr\right) \end{aligned}\right\} \quad . \quad . \quad . \quad (3)$$

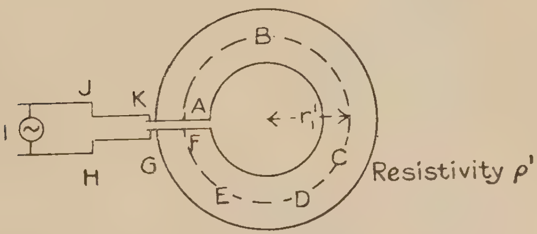
The radial distribution of current in the inductor is itself indeterminate without some specification of the type of generator connected thereto.

We shall therefore make the following stipulation:—

> The inductor shall consist of one turn, complete, save for an infinitesimal gap, in which the condenser is placed (fig. 1).

The generator we assume connected to the perfectly conducting condenser plates A, F, and to be such that the current flowing in it and its leads produces no appreciable electric force, *qua* current, except in the region HIJ, and that the currents flowing in the inductor produce no electric force in the region GHIJK. Further, the magnetic field in the region HIJ shall be such that the line integral of the

Fig. 1.



total electric force, E_t, round GHIJKG shall be V_t. The generator shall have no resistance. Then $\int_F^A E_t\,ds_{(s=AF)}$ will, if the gap be sufficiently small, be independent of the position of the terminal points A, F, on the condenser plates. It is determined principally by the charges on the plates, and Lt gap$\to 0$ to a negligible extent by the part of E_t due to the currents, ABCDEF, *qua* currents, and will therefore be V_t, for all terminal points, A, F, on the condenser plates.

Notation.

Total electric force at time t .... E_t :
alternatively, real part of $E\,\epsilon^{ipt}$ E.M.U.

Total magnetic force .... H_t :
alternatively, real part of $H\,\epsilon^{ipt}$,,

Total magnetic induction .... B_t :
alternatively, real part of $B\,\epsilon^{ipt}$,,

Generator voltage, at time t .... V_t :
alternatively, real part of $V\,\epsilon^{ipt}$,,

A certain change therein .... v_t :
alternatively, real part of $v\,\epsilon^{ipt}$,,

Current density—inductor .... j_t' :
alternatively, real part of $j'\epsilon^{ipt}$,,

Current density—charge .... j_t :
alternatively, real part of $j\,\epsilon^{ipt}$,,

Pulsatance	p radians sec.$^{-1}$.
Time	t sec.
Permeability—inductor, assumed unity.	
Permeability—charge	μ.
Resistivity—inductor	ρ' E.M.U.
Resistivity—charge	ρ ,,
Axial length—inductor	l' cm.
Axial length—charge	l ,,
Radius—inductor, outer	R_2 ,,
Radius—inductor, variably	r_1' and r' cm.
Radius—inductor, inner	R_1 cm.
Radius—charge, outer	R ,,
Radius—charge, variably	r_1 and r cm.
Radius—charge, inner assumed zero.	

Sign convention : E, j, j' positive measured clockwise round H+, or B+.

Parameters :

$$i=\sqrt{-1},\quad \beta=\sqrt{\rho/4\pi ip\mu},\qquad \alpha=\sqrt{-\rho/4\pi ip\mu},$$
$$\beta'=\sqrt{\rho'/4\pi p},\qquad \alpha'=\sqrt{-\rho'/4\pi ip}.$$

With the above notation, we may write the first of Maxwell's equations in integral form as

$$\frac{d}{dt}\int_{(\sigma)} B_t\,d\sigma=-\int_{(s)}\rho j_t\,ds,\quad (0<r_1<R)\quad .\quad .\quad .\quad (4\,a)$$

the circuit s, enclosing the area σ, being in the charge, or

$$\frac{d}{dt}\int_{(\sigma)} B_t\,d\sigma=-\int_{(s)}\rho' j_t'\,ds-V_t,\quad (R_1<r_1'<R_2)\quad (4\,b)$$
$$(\sigma=ABCDEA)\quad (s=ABCDE)$$

the circuit s, enclosing the area σ, now being in the inductor.

We shall further find it necessary to assume that the current density at a given radius is the same at all parts of the circumference. That is, we assume the frequency to be low compared with the gravest mode of free electrical oscillation of the inductor itself, in the absence of condenser or generator. The current will then be determined principally by the coefficients of inductance of the system, and to a negligible extent by the coefficients of capacity.

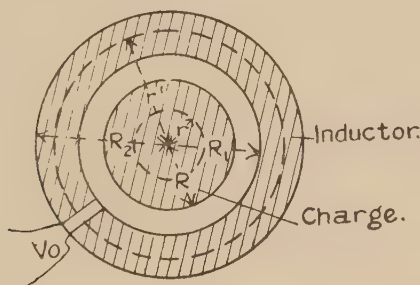
We may then write the second of Maxwell's equations as

$$\operatorname{curl} \mathrm{H}_t = 4\pi j_t, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the term $+\frac{1}{c}\frac{d\mathrm{E}_t}{dt}$ being, *a fortiori*, dropped, in view of the above frequency restriction.

To bring the problem within the sphere of tractable analysis we consider a cylindrical charge, long compared with its radius, placed coaxially in a long single-turn inductor. It will then be unnecessary to make any approximations regarding the distribution of current or flux that general theory might have suggested until the rigid solution has been written down—a procedure desirable in every analysis.

Fig. 2.



Considering the case of the loaded inductor, of which fig. 2 is a section, it will be seen that (5) can be written

$$\left.\begin{aligned} \mathrm{H}_{r_1 t} &= 4\pi \int_{r_1}^{\mathrm{R}} j_t \, dr + 4\pi \int_{\mathrm{R}_1}^{\mathrm{R}_2} j_t' \, dr', \quad (0 < r_1 < \mathrm{R}_1) \\ \mathrm{H}_{r_1' t} &= 4\pi \int_{r_1'}^{\mathrm{R}_2} j_t' \, dr \qquad\qquad\qquad\quad (\mathrm{R} < r_1' < \mathrm{R}_2) \end{aligned}\right\} \quad (6)$$

in integral form, and (4) becomes

$$\frac{d}{dt}\left[4\pi^2 \mu r_1^2 \int_{\mathrm{R}_1}^{\mathrm{R}_2} j_t' \, dr' + 4\pi^2 \mu \int_{r_1}^{\mathrm{R}} j_t r_1^2 \, dr + 4\pi^2 \mu \int_0^{r_1} j_t r^2 \, dr\right]$$
$$= -2\pi \rho r_1 j_t \quad (0 < r_1 < \mathrm{R}) \quad . \quad (7\,a)$$

in the charge, while for the inductor we have

$$\frac{d}{dt}\left[4\pi^2(\mu - 1)\mathrm{R}^2 \int_{\mathrm{R}_1}^{\mathrm{R}_2} j_t' \, dr' + 4\pi^2 r_1'^2 \int_{r_1}^{\mathrm{R}_2} j_t' \, dr' + 4\pi^2 \mu \int_0^{\mathrm{R}} j_t r^2 \, dr\right]$$
$$= -2\pi \rho' r_1' j_t' + \mathrm{V}_t. \quad (\mathrm{R}_1 < r_1' < \mathrm{R}_2) \quad (7\,b)$$

The third integral on the L.H.S. of (7 *b*), which represents the contribution due to the charge, to the total flux linking the ring r_1', is independent of r_1'. The introduction of the charge can therefore be compensated by an addition to V_t independent of r_1', given by

$$v_t = \frac{d}{dt}\int_0^{R} \mu\, 4\pi^2 r^2 j_t\, dr + \frac{d}{dt}(\mu-1)\, 4\pi^2 R^2 \int_{R_1}^{R_2} j_t'\, dr'.$$

In other words, if we circulate unit total current (per unit length) $\left(\left|\int_{R_1}^{R_2} j_t'\, dr'\right| = 1\right)$, the loss in the inductor is not influenced by the presence of the charge, since the current density is, in both cases, the same function of the radius.

Representing all the electric quantities by complexes, we define the total current in a thick inductor (per unit length) as

$$I = \int_{R_1}^{R} j'\, dr, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

we have from (2), since V and v are independent of r,

$$\left.\begin{aligned} P_d &= \text{real part of } \tfrac{1}{2}(\tilde{\tilde{V}}I + \tilde{v}I), \\ P_c &= \quad ,, \quad ,, \quad ,, \quad \tfrac{1}{2}i(\tilde{\tilde{V}}I + \tilde{v}I), \end{aligned}\right\} \quad . \quad . \quad . \quad (9)$$

We can now re-write (7 *a*) and (7 *b*) as

$$r_1^2 I + r_1^2 \int_{r_1}^{R} j\, dr + \int_0^{r_1} j r^2\, dr = \frac{-\rho r_1 j}{2\pi i p \mu} \quad (0 < r_1 < R) \quad . \quad (10\,a)$$

and

$$4\pi^2(\mu-1)R^2 \int_{R_1}^{R_2} j'\, dr' + 4\pi^2 r_1^2 \int_{r_1'}^{R_2} j'\, dr' + 4\pi^2 \int_{R_1}^{r_1'} j' r'^2\, dr'$$

$$+ 4\pi^2\mu \int_0^{R} j r^2\, dr = -\frac{2\pi\rho' r_1' j' - V}{ip}; \quad (R_1 < r_1' < R_2). \quad (10\,b)$$

For the empty inductor, (10 *b*) becomes

$$4\pi^2 \int_{R_1}^{r_1'} j' r'^2\, dr' + 4\pi^2 r_1'^2 \int_{r_1'}^{R_2} j'\, dr' = \frac{V}{ip} - \frac{2\pi\rho' j' r_1'}{ip}, \quad (10\,c)$$

the solution of which is

$$j' = \lambda \, . \, J_1\left(\frac{r'}{\alpha'}\right) + \nu Y_1\left(\frac{r'}{\alpha'}\right), \quad . \quad . \quad . \quad (11)$$

where J_1 and Y_1 are Bessel functions of order unity and λ and ν are chosen to satisfy (10) at the boundaries $r_1 = R$, $r' = R_2$.

Substituting for j' and putting $r'=R_1$, we get

$$4\pi^2 R_1^2 \int_{R_1}^{R_2} \left\{ \lambda J_1\left(\frac{r'}{\alpha'}\right) + \nu Y_1\left(\frac{r'}{\alpha'}\right) \right\} dr'$$
$$= \frac{V}{ip} - \frac{2\pi\rho'}{ip} . R_1 \left\{ \lambda J_1\left(\frac{R_1}{\alpha'}\right) + \nu Y_1\left(\frac{R_1}{\alpha'}\right) \right\},$$

i. e.

$$\alpha' 4\pi^2 R_1^2 \left[\lambda \left\{ J_0\left(\frac{R_1}{\alpha'}\right) - J_0\left(\frac{R_2}{\alpha'}\right) \right\} + \nu \left\{ Y_0\left(\frac{R_1}{\alpha'}\right) - Y_0\left(\frac{R_2}{\alpha'}\right) \right\} \right]$$
$$= \frac{V}{ip} - \frac{2\pi\rho'}{ip} . R_1 \left\{ \lambda J_1\left(\frac{R_1}{\alpha'}\right) + \nu Y_1\left(\frac{R_1}{\alpha'}\right) \right\},$$

which rearranges, since

$$J_2\left(\frac{R}{\alpha}\right) = -J_0\left(\frac{R}{\alpha}\right) + \frac{2\alpha}{R} J_1\left(\frac{R}{\alpha}\right),$$

and similarly for Y_2, as

$$\lambda R_1^2 \left\{ J_0\left(\frac{R_2}{\alpha'}\right) + J_2\left(\frac{R_1}{\alpha'}\right) \right\} + \nu R_1^2 \left\{ Y_0\left(\frac{R_2}{\alpha'}\right) + Y_2\left(\frac{R_1}{\alpha'}\right) \right\}$$
$$= \frac{V}{4\pi^2 ip\alpha'} . \quad . \quad (12)$$

Putting $r=R_2$ we have

$$4\pi^2 \int_{R_1}^{R_2} j' r'^2 dr' = \frac{V}{ip} - \frac{2\pi\rho'}{ip} . R_2 \left\{ \lambda J_1\left(\frac{R_2}{\alpha'}\right) + \nu Y_1\left(\frac{R_2}{\alpha'}\right) \right\},$$

i. e.

$$\lambda \left\{ R_2^2 J_2\left(\frac{R_2}{\alpha'}\right) - R_1^2 J_2\left(\frac{R_1}{\alpha'}\right) \right\} + \nu \left\{ R_2^2 Y_2\left(\frac{R_2}{\alpha'}\right) - R_1^2 Y_2\left(\frac{R_1}{\alpha'}\right) \right\}$$
$$= \frac{V}{4\pi^2 ip\alpha'} + 2\alpha' R_2 \left\{ \lambda J_1\left(\frac{R_2}{\alpha'}\right) + \nu Y_1\left(\frac{R_2}{\alpha'}\right) \right\},$$

which also rearranges, giving

$$\lambda \left\{ R_1^2 J_2\left(\frac{R_1}{\alpha'}\right) + R_2^2 J_0\left(\frac{R_2}{\alpha'}\right) \right\} + \nu \left\{ R_1^2 Y_2\left(\frac{R_1}{\alpha'}\right) + R_2^2 Y_0\left(\frac{R_2}{\alpha'}\right) \right\}$$
$$= V/4\pi^2 ip\alpha' . \quad . \quad (13)$$

Subtracting (13) from (12), we obtain

$$\lambda . J_0\left(\frac{R_2}{\alpha'}\right) + \nu Y_2\left(\frac{R_2}{\alpha'}\right) = 0. \quad . \quad . \quad . \quad . \quad (14)$$

Writing $$J_0\left(\frac{R_2}{\alpha'}\right)+J_2\left(\frac{R_1}{\alpha'}\right)=a$$

and $$Y_0\left(\frac{R_2}{\alpha'}\right)+Y_2\left(\frac{R_1}{\alpha'}\right)=b,$$

and substituting (14) in (12), we find

$$\lambda\left\{a-\frac{J_0\left(\frac{R_2}{\alpha'}\right)}{Y_0\left(\frac{R_2}{\alpha'}\right)}.b\right\}=V/4\pi^2 ip\alpha',$$

or $$\lambda=\frac{V}{4\pi^2 R_1^2 ip\alpha' d}J_0\left(\frac{R_2}{\alpha'}\right), \quad . \quad . \quad . \quad (15)$$

$$\nu=\frac{V}{4\pi^2 R_1^2 ip\alpha' d}Y_0\left(\frac{R^2}{\alpha'}\right), \quad . \quad . \quad . \quad (16)$$

where $$d=a\,Y_0\left(\frac{R_2}{\alpha'}\right)-b\,J_0\left(\frac{R_2}{\alpha'}\right),$$

i. e.

$$d=Y_0\left(\frac{R_2}{\alpha'}\right)\left\{J_0\left(\frac{R_2}{\alpha'}\right)+J_2\left(\frac{R_1}{\alpha'}\right)\right\}$$
$$-J_0\left(\frac{R_2}{\alpha'}\right)\left\{Y_0\left(\frac{R_2}{\alpha'}\right)+Y_2\left(\frac{R_1}{\alpha'}\right)\right\}$$
$$=Y_0\left(\frac{R_2}{\alpha'}\right)J_2\left(\frac{R_1}{\alpha'}\right)-J_0\left(\frac{R_2}{\alpha'}\right)Y_2\left(\frac{R_1}{\alpha'}\right).$$

Write $$A=\overline{V}^2/4\pi^2 R_1^2 ip,$$

$\overline{V}^2$ being written for the time average of V_t^2, i. e. $\frac{V^2}{2}$ (and similarly with $\overline{I}^2$). Then (*cf.* treatment of the thin inductor, above)

$$\frac{1}{2}\int_{R_1}^{R_2}\tilde{V}j'\,dr'=-\frac{A}{d}\,Y_0\left(\frac{R_2}{\alpha'}\right)\left\{-J_0\left(\frac{R_2}{\alpha'}\right)+J_0\left(\frac{R_1}{\alpha'}\right)\right\}$$
$$+\frac{\alpha A}{d}.J_0\left(\frac{R_2}{\alpha'}\right)\left\{-Y_0\left(\frac{R_2}{\alpha'}\right)+Y_0\left(\frac{R_1}{\alpha'}\right)\right\}$$
$$=\frac{A}{d}\left\{J_0\left(\frac{R_2}{\alpha'}\right).Y_0\left(\frac{R_1}{\alpha'}\right)-Y_0\left(\frac{R_2}{\alpha'}\right).J_0\left(\frac{R_1}{\alpha'}\right)\right\}$$
$$=A.\frac{J_0\left(\frac{R_2}{\alpha'}\right).Y_0\left(\frac{R_1}{\alpha'}\right)-Y_0\left(\frac{R_2}{\alpha'}\right).J_0\left(\frac{R_1}{\alpha'}\right)}{Y_0\left(\frac{R_2}{\alpha'}\right).J_2\left(\frac{R_1}{\alpha'}\right)-J_0\left(\frac{R_2}{\alpha'}\right).Y_2\left(\frac{R_1}{\alpha'}\right)};$$
$$. \quad . \quad . \quad . \quad . \quad (17)$$

dividing top and bottom by $J_0\left(\frac{R_1}{\alpha'}\right) \cdot Y_0\left(\frac{R_1}{\alpha'}\right)$, we have

$$\frac{1}{2}\int_{R_1}^{R_2} \tilde{V} j' \, dr' = -A \cdot \frac{\dfrac{J_0\left(\frac{R_2}{\alpha'}\right)}{J_0\left(\frac{R_1}{\alpha'}\right)} - \dfrac{Y_0\left(\frac{R_2}{\alpha'}\right)}{Y_0\left(\frac{R_1}{\alpha'}\right)}}{\dfrac{J_0\left(\frac{R^2}{\alpha'}\right)}{J_0\left(\frac{R_1}{\alpha'}\right)} \cdot \dfrac{Y_2\left(\frac{R_1}{\alpha'}\right)}{Y_2\left(\frac{R_1}{\alpha'}\right)} - \dfrac{Y_0\left(\frac{R_2}{\alpha'}\right) \cdot J_2\left(\frac{R_1}{\alpha'}\right)}{Y_0\left(\frac{R_1}{\alpha'}\right) \; J_0\left(\frac{R_1}{\alpha'}\right)}} . \quad . \; . \; . \; (18)$$

Since the inductor is made of copper ($\rho' = 1 \cdot 7 \times 10^3$) and is of necessity several centimetres in radius, the value of R_1'/β' at the frequency we contemplate (many thousand cycles per second) is of the order of several hundred. We may therefore write with considerable accuracy:

$$Y_2\left(\frac{R_1}{\alpha'}\right) \Big/ Y_0\left(\frac{R_1}{\alpha'}\right) = J_2\left(\frac{R_1}{\alpha'}\right) \Big/ J_0\left(\frac{R_1}{\alpha'}\right)$$

$$= -1 + i\beta' \sqrt{2}(1+i) / R_1. \quad . \; (19)$$

Again, since

$$R_1/\beta' \gg 1 \, . \, J_0\left(\frac{R_2}{\alpha'}\right) \Big/ J_0\left(\frac{R_1}{\alpha'}\right) \simeq Y_0\left(\frac{R_2}{\alpha'}\right) \Big/ Y_0\left(\frac{R_1}{\alpha'}\right) \cdot \epsilon^{2(R_2 - R_1)/\beta'}.$$

The inductor can always be made so thick that $\epsilon^{2(R_2 - R_1)/\beta'}$ is very large. We are therefore justified in writing

$$\frac{1}{2}\int_{R_1}^{R_2} \tilde{V} j' \, dr' = A / \{1 - i\beta' \sqrt{2}(1+i)/R_1\}$$

to an accuracy exceeding $\{1 + \epsilon^{-2(R_2 - R_1)/\beta'}\} : 1$

$$= A \left\{1 + \frac{\beta' \sqrt{2}}{R_1} + \frac{\beta' \sqrt{2}}{R_1} \cdot i\right\} \Big/ \left\{\left(1 + \frac{\beta' \sqrt{2}}{R_1}\right)^2 + \frac{2\beta'^2}{R_1^2}\right\}$$

$$= \frac{\bar{V}^2}{4\pi^2 p \, R_1^2}\left(\frac{\beta' \sqrt{2}}{R_1} - i\right), \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (20)$$

on neglecting $2\sqrt{2}\,\beta'/R_1$ compared with unity and replacing A.

We therefore have for the power supplied to the empty inductor

$$\frac{\beta' \sqrt{2}}{4\pi^2 p \, R_1^3} \bar{V}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1}, \quad . \; . \; . \; . \; (21)$$

and for the conserved power

$$\frac{1}{4\pi^2 p \mathrm{R}_1^2} \overline{\mathrm{V}}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1}. \quad (22)$$

the "power ratio," *i. e.* $\dfrac{\text{Dissipated Power}}{\text{Conserved Power}}$, being

$$\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{\mathrm{R}_1} \sqrt{\rho'/p}. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

As the "power ratio" is small (seldom greater than 10^{-2}) we may take the inductor current as

$$\frac{\text{Conserved Power}}{\mathrm{V}_0}, \quad i.e.\ \overline{\mathrm{I}} = \overline{\mathrm{V}}/4\pi^2 p \mathrm{R}_1^2,$$

and the error will seldom exceed one part in 20,000.

We can thus write (21) and (22) in terms of the inductor current I per unit length:

$$\frac{4\pi^2 \mathrm{R}_1 \sqrt{p\rho'}}{\sqrt{2\pi}} \overline{\mathrm{I}}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1} \quad . \quad . \quad . \quad (24)$$

and

$$4\pi^2 p \mathrm{R}_1^2 \overline{\mathrm{I}}^2 \text{ erg sec.}^{-1} \text{ cm.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

We now calculate v, the necessary change in V, due to the introduction of the charge.

Reverting to equation $(10a)$,

$$r_1^2 \mathrm{I} + r_1^2 \int_{r_1}^{\mathrm{R}} j\, dr + \int_0^{r_1} j r^2\, dr = -\frac{\rho r_1 j}{2\pi i p \mu}, \quad (0 < r_1 < \mathrm{R})$$

the solution is

$$j = \frac{\mathrm{I}}{\alpha} \mathrm{J}_1\left(\frac{r}{\alpha}\right) \Big/ \mathrm{J}_0\left(\frac{\mathrm{R}}{\alpha}\right), \quad . \quad . \quad . \quad . \quad . \quad (26)$$

where

$$\alpha = \sqrt{-\rho/4\pi i p \mu}$$

and J_1 and J_0 are Bessel functions of the first and zeroth order.

Now

$$v = i p \mu \int_0^{\mathrm{R}} 4\pi^2 r^2 j\, dr + (\mu - 1)\, i p\, 4\pi^2 \mathrm{R}^2 \mathrm{I},$$

as has been noted.

Inserting the value for j, we get

$$\tfrac{1}{2}\tilde{v}\,\mathrm{I}=\overline{\left[\frac{2\pi^2\mu\,ip\,\mathrm{I}}{\alpha\,\mathrm{J}_0\left(\frac{\mathrm{R}}{\alpha}\right)}\cdot\int_0^{\mathrm{R}} r^2\mathrm{J}_1\left(\frac{r}{\alpha}\right)dr\right]}\mathrm{I}-(\mu-1)\,ip\,4\pi^2\mathrm{R}^2\bar{\mathrm{I}}^2 \quad . \quad . \quad . \quad (27)$$

$$=\overline{\left[-4\pi^2 ip\mu\,\mathrm{I}^2\left[\mathrm{R}^2-2\mathrm{R}\alpha\mathrm{J}_1\left(\frac{r}{\alpha}\right)\Big/\mathrm{J}_0\left(\frac{\mathrm{R}}{\alpha}\right)\right]\right]}$$

$$-(\mu-1)\,ip\,4\pi^2\mathrm{R}^2\bar{\mathrm{I}}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$\frac{1}{2}\int_{\mathrm{R}_1}^{\mathrm{R}_2}\tilde{v}\mathrm{I}=\frac{4\pi^2 p\mu\bar{\mathrm{I}}^2}{\mathrm{ber}^2\frac{\mathrm{R}}{\beta}+\mathrm{bei}^2\frac{\mathrm{R}}{\beta}}\left[2\beta\mathrm{R}\left(\mathrm{ber}\frac{\mathrm{R}}{\beta}\,\mathrm{ber}'\frac{\mathrm{R}}{\beta}+\mathrm{bei}\frac{\mathrm{R}}{\beta}\,\mathrm{bei}'\frac{\mathrm{R}}{\beta}\right)\right.$$

$$\left.+i\left\{\mathrm{R}^2-2\beta\mathrm{R}\left(\mathrm{ber}'\frac{\mathrm{R}}{\beta}\,\mathrm{bei}\frac{\mathrm{R}}{\beta}-\mathrm{bei}'\frac{\mathrm{R}}{\beta}\,\mathrm{ber}\frac{\mathrm{R}}{\beta}\right)\right\}\right]$$

$$-(\mu-1)\,ip\,4\pi^2\mathrm{R}^2\bar{\mathrm{I}}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

By [9] the real part of (29) gives the extra power absorbed by the inductor (carrying unit current), when the charge is inserted, and the coefficient of i in (29) taken negatively gives extra conserved power absorbed by the loaded inductor. (For unit current, this is its change of reactance.)

Two special cases of this formula are of interest: Firstly, when R/β approaches zero (and very approximately when $\mathrm{R}/\beta<1$); secondly, when R/β approaches infinity (and very approximately when $\mathrm{R}/\beta>3$).

First Case. ($\mathrm{R}/\beta<1$.)

In this case the expression for the power reduces to

$$2\pi^3p^2\mathrm{R}^4\frac{\mu^2}{\rho}\bar{\mathrm{I}}^2 \text{ erg sec.}^{-1}\text{ cm.}^{-1}. \quad . \quad . \quad . \quad (30)$$

The expression (30) represents the well-known facts of low frequency induction, *e. g.* the heating of transformer cores. It will be noticed, however, that the criterion of its applicability is that R/β should be less than 1 and not that the frequency, *per se*, should be low. Actually, the parameters of the determining function are no fewer than four, e. s. ρ, R, μ, p. The looseness of the term "low frequency induction" is therefore apparent, and it is more reasonable to refer to this class of phenomena as "volume induction," since the criterion $\mathrm{R}/\beta>1$ is tantamount to saying that the current density is proportional to the radius, *i. e.* the skin effect is not marked. Under these circumstances, the heating

is decreased in the ratio $n:1$ if a charge consisting of one cylinder of radius R is divided into n cylinders of radius $R/\sqrt{n}$.

The conserved power in the charge (which, taken negatively, for unit current per unit length, is the inductor reactance abolished by the charge), is

$$4\pi^2 p R^2(\mu-1). \quad (\mu >> 1) \quad . \quad . \quad (31)$$

If $\mu=1$, the charge reactance is negligible compared with its resistance (both referred to the inductor).

Second Case. $(R/\beta > 3.)$

As in the first case, the criterion of applicability is not frequency alone.

We prefer therefore to refer to this condition as "surface" rather than "high frequency" induction heating, since when $R/\beta > 3$, the heat generation is confined substantially to the surface of the charge.

The power may be written

$$\overline{I^2}\, 2\sqrt{2\pi} \,.\, R\sqrt{p\rho\mu} \text{ erg sec.}^{-1} \text{ cm.}^{-1}, \quad . \quad . \quad (32)$$

from which it follows that the effect of division of the charge, as above, is to increase the heating $\sqrt{n}$ times.

The conserved power may be written

$$-4\pi^2 R^2 p \overline{I^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

It may be noted that $\underset{p\to\infty}{\mathrm{Lt}}$ the ratio of power : conserved power $\propto 1/\sqrt{p}$, being in fact

$$\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{R}\sqrt{\rho/p},$$

a result which, needless to say, contradicts Dr. Northrup's * rather obscure statement that "when the frequency is sufficiently high to justify the assumptions" (which are not clearly stated) "the resistance of a charge is equal to its reactance."

We have seen that at the frequencies which we contemplate, the inductor loss varies as $\sqrt{p}$. $(R_1/\beta >> 3)$. If in the charge $(R/\beta < 1)$, the efficiency is

$$\eta = p^2 R^4 \mu^2 l \,/\, \{p^2 R^4 \mu^2 l + \rho\sqrt{2} R_1 \sqrt{p\rho'}\, l'\}, \quad . \quad (34)$$

account being now taken of the different lengths of inductor

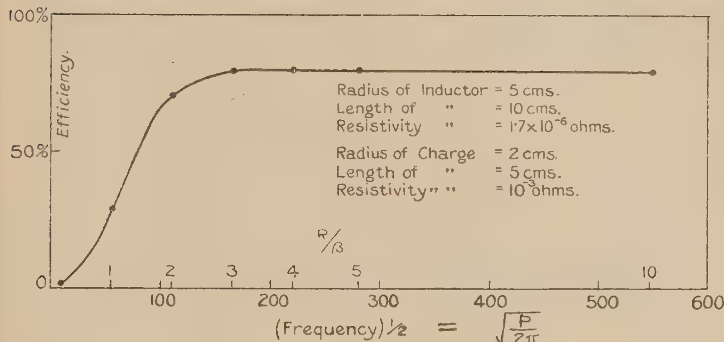
* Northrup, *loc. cit.*

and charge. η may therefore be raised by raising the frequency until when $R/\beta > 3$, it becomes independent of frequency and is in fact

$$\eta = lR\sqrt{\rho} / \{lR\sqrt{\rho} + l'R_1\sqrt{\rho'}\}. \quad . \quad . \quad (35)$$

The exact dependence of η on p is shown in the curve, fig. 3, the simple formula (21) being used for the inductor ($R_1/\beta >> 3$), while the rigid expression (29) is used for the charge.

Fig. 3.



It is clear, then, that the efficiency is maximal if $R/\beta > 3$ in the charge. This implies $R_1/\beta > 3$ in the inductor, since R cannot exceed R_1, and will in general be several centimetres less, moreover ρ will generally exceed ρ'. (The charge, even if of copper, will, let us hope, be hot.)

The fact that the necessary and sufficient criterion for maximal efficiency is $R/\beta > 3$ in the charge, is a result of considerable interest, and universal application. It may theoretically be possible to improve on this maximal efficiency by winding the inductor with divided wire, though Professor Howe has shown * that this must be used with a nice discrimination. He points out that when R_1/β' is large (it is always of the order of several hundred) and $(R_2 - R_1)/\beta' > 3$, multi-layer coils are definitely a mistake, and are in fact only justifiable if $(R_2 - R_1)/\beta < 1$.

In any case the difficulties of cooling a multi-layer inductor are very great, and actually the only practical form of inductor is a closely wound single-layer coil, of square copper tube, through which water may be circulated.

Considering such an inductor from the point of view of losses we are only interested in the thickness of the inner

* G. W. O. Howe, J. I. E. E. lviii. p. 152 (1920); P. R. S., xciii. (1917).

wall, since it was shown that when $(R_2 - R_1)/\beta' > 3$, the losses are substantially independent of R_2. Taking 10,000 cycles as a minimum frequency, we find $(R_2 - R_1)$ of the order of 1 mm. At one million cycles it would be of the order of $\frac{1}{10}$ mm.

It will be of interest to consider the frequency which gives maximal heating in several special cases. For instance, consider a charge 3 cm. in radius and we should have for copper $p > 1{\cdot}5 \times 10^2$ sec.$^{-1}$, for carbon $p > 4 \times 10^5$ sec.$^{-1}$, and for silicon $p > 10^6$ sec.$^{-1}$. It is only when we have to heat very small charges of high resistivity that very high frequencies are desirable.

The effect of permeability affords interesting grounds for speculation. As in iron at high frequency the skin is extremely marked, hysteresis, which is a volume effect, should play a comparatively insignificant part. We must assume that the great efficiencies which are so easily obtained with iron below its magnetic change point must be accounted for almost wholly by its permeability. Experiments with iron indicated an average permeability of the order of 1000 at 10^6 cycles, a fact which seems to bear out the general observations of E. F. W. Alexanderson.

Choice of Frequency.

Under almost all practical circumstances the frequency need not exceed 10^4 cycles/sec. and will in general be determined by the type of generator available. There is, however, one point worth noting in this connexion. The "power ratio" becomes proportional to the square root of the frequency, so that "conserved power" which the condenser is called upon to deal with will ultimately become at sufficiently high frequencies a matter of considerable concern, owing to ohmic loss in the electrodes and dielectric hysteresis. All things considered, therefore, it is desirable to work at frequencies exceeding by as little as possible that which makes $R/\beta = 3$ in the charge.

Conclusions.

It has been shown that there is a limit to the maximal efficiency of which an inductor coil is capable depending on its dimensions and on the dimensions and resistance of the charge; in the case of a cold copper charge, this maximal efficiency cannot exceed 50 per cent. It is further shown that the necessary and sufficient criterion for maximal efficiency is $R/\beta > 3$ in the charge, and that while increase

of frequency generally allows of a smaller condenser capacity, at the same time it increases the conserved power.

The ultimate choice of frequency in any particular case must therefore rest on commercial considerations regarding the cost of condensers and generators subject only to the condition $R/\beta > 3$ in the charge.

The authors wish to thank Professor C. G. Darwin, F.R.S., and Professor C. E. Inglis, M.A., M.I.C.E., for their kind encouragement and valuable criticism, and Mr. A. P. M. Fleming, C.B.E., M.I.E.E., Manager, Research and Education Departments, Metropolitan-Vickers Electrical Company Limited, for permission to publish this investigation.

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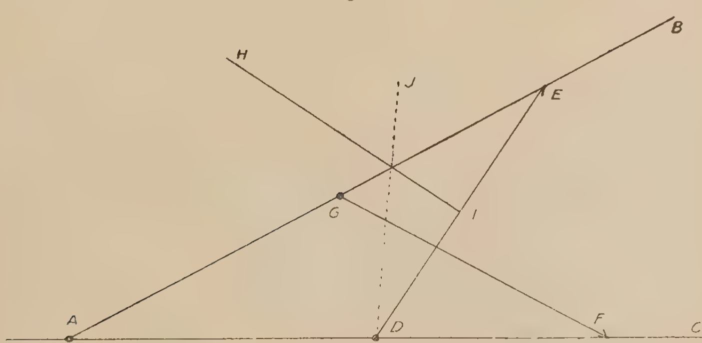
Metropolitan-Vickers Electrical Co. Ltd.,
Trafford Park, Manchester.
November 21, 1925.

LXXI. *The Mechanical Solution of some Geometrical Problems.* *By* H. R. Kempe, *M.Inst.C.E.**

As shown by fig. 1, AB and AC are two links linked together at A; GF is a link linked to AB at G, and

Fig. 1.



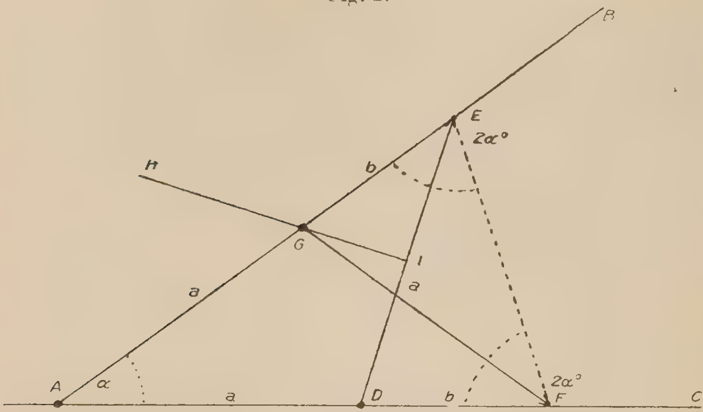
DE a similar link linked to AC at D; the ends of these links—E and F—slide on AB and AC respectively. Fixed to link DE and at right angles to it, at the midway point I, is a bar IH which can slide over AB.

* Communicated by the Author.

The lengths AD, AG, DE, and GF are all equal, HI may be any length.

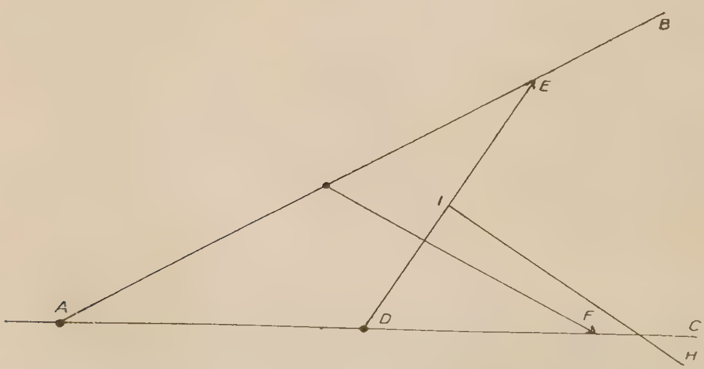
If, now, E and F be slid along AB and AC respectively, until HI comes on the point G, as shown by fig. 2, then the

Fig. 2.



triangle AEF will be formed, and this triangle will have each of the angles E and F to be *twice* the angle A, as in the case of Prop 10, Book IV, Euclid.

Fig. 3.



Now turn over the bar HI, as shown in fig. 3, and slide E and F along AB and AC respectively until the end F of

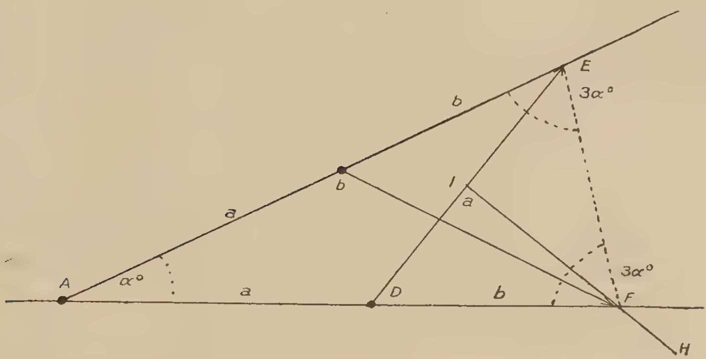
GF comes against HI, as shown by fig. 4, then triangle AEF will be formed, and this triangle will have each of the angles E and F to be *thrice* the angle A, a result which has no Euclidean solution.

It may be stated that in the case fig. 2,

$$\frac{b^2}{a}=a+b,$$

from which the ratio of a to b can be determined; but in

Fig. 4.



the case, fig. 4,

$$\frac{a^2}{b^2}=\frac{2a+b}{a+b},$$

which is a cubic equation and cannot be solved by Euclidean geometry.

In reference to fig. 1 it may be mentioned that the angle JDE is one third of the angle JDC, so that the arrangement affords a means of trisecting an angle. To do this E would be slid along AB until the intersection of AB and HI comes on the line JD, JDC being the angle to be trisected; this is practically the same solution as that which was given by the author in vol. xxvi. July 1918 of this Magazine.

Brockham, Betchworth,
Surrey.

LXXII. *The Forces of Chemical Affinity. A Study of Crystal Structure in the Light of the New Atomic Models.* By ALBERT C. CREHORE *.

SINCE the last paper † was communicated the general expression for the electrostatic force acting upon a first electron due to a second situated in any position whatever has been obtained. The so-called "circle-and-point" approximation to the oblate spheroid of the electron has been employed throughout. In that paper the discussion was limited to electrons having parallel axes, and this restriction of course prevented any consideration of crystal structure. General formulæ are required before a study of the grouping of atoms in a space lattice can be undertaken, because the axes of all electrons and of all atoms are not parallel to each other.

The process of finding the force upon a first atom due to a second atom is evidently merely one of summation after the force between individual electrons has been obtained—that is to say, summing the forces between the individual charges composing the atoms, taking one from each atom at a time. As between two hydrogen atoms each containing three individual bodies, two negative electrons and one positive charge of $2e$, this process requires $3\times 3=9$ expressions to be summed, while for two carbon atoms consisting of 15 charges each according to the model ‡, fig. 3, twelve electrons and three positive charges of $4e$ each, there are $15\times 15=225$ expressions to be summed. These expressions have been obtained both for two hydrogen atoms and for two carbon atoms in accordance with the models of these atoms, but their derivation is deferred for a subsequent communication. We are now concerned with their applications to crystal structure.

Although the crystal structure of solid hydrogen has never been experimentally determined, yet we shall give some space here to its consideration because the atom of hydrogen is far the simplest atomic form. It is hoped that this theoretical discussion may encourage those who have the laboratory equipment to undertake the X-ray examination of solid hydrogen, though the many difficulties are keenly realized, the work necessitating operations at very low temperatures.

* Communicated by the Author.

† A. C. Crehore, Phil. Mag. May 1925, p. 839.

‡ A. C. Crehore, Phil. Mag. May 1922, p. 886.

There are many forms of space lattice in which different substances are known to crystallize, but there are four of them in particular that we shall consider both because of their common occurrence and their greater simplicity. These are (1) the simple cubic lattice, (2) the so-called face-centred cubic lattice, (3) the body-centred cubic lattice, and (4) two interpenetrating face-centred lattices such as the diamond.

In addition to the information afforded by the ordinary X-ray analysis of a crystal, which merely gives the locations of the centres of each atom, much more is required before any theoretical investigation of the electrostatic forces between the atoms can be undertaken. These depend fully as much upon the relative orientations of the axes of the atoms as upon their mutual distances. But the orientation of the axis of an atom depends primarily upon the electromagnetic forces due to the rotation of the fundamental charges within it, while it is only the translational forces that have a purely electrostatic character. In other words, as between two atoms there exists a mutual electromagnetic torque tending to bring their two axes into parallelism. The magnitude of this torque increases at first with an increase in the angle between their axes, and is in fact a function of this angle.

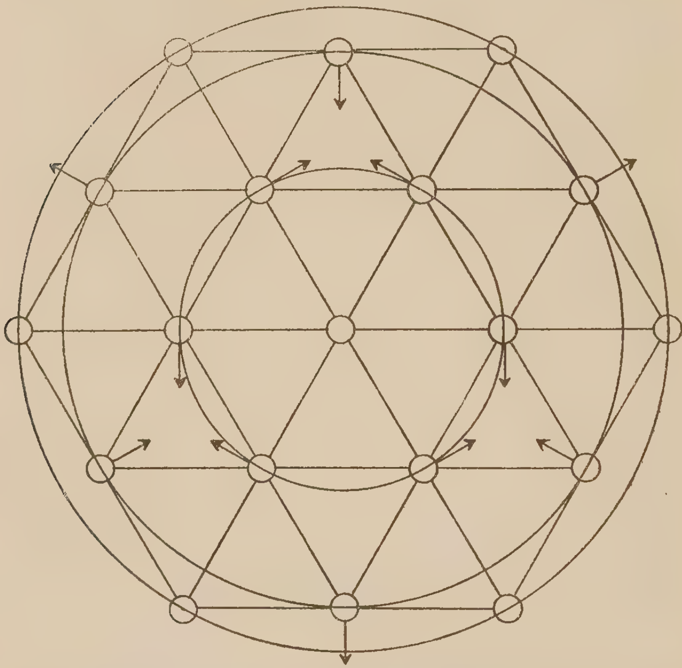
Although the form of atomic model now under discussion differs materially from that presented * in 1915, yet in this matter of the turning moments of the force there is no essential difference. The centres of the electrons within the atoms in the models here discussed remain in stationary positions at the absolute zero of temperature, each merely rotating upon its own axis, while the electrons considered in that paper were supposed to revolve in orbits. In either case the rotation or the orbital revolution brings about the same result, a tendency to bring the two axes into parallelism. On p. 776 of the June paper referred to, the question of the equilibrium of turning moments of the forces in a lattice of atoms upon any selected atom is presented, and this reasoning applies with equal force to the new form of atom, it being independent of the translational forces. In fact, from the standpoint of the moments of the forces alone it may be shown that the axes of the atoms can take but four different directions in any lattice belonging to the cubic system of crystals, namely parallel to the four diagonals

* A. C. Crehore, Phil. Mag. June 1915, p. 750; Phil. Mag. Aug. 1915, p. 257.

of a cube, or to the four medial lines of a regular tetrahedron. The whole lattice is thereby divided into four equal groups of atoms, there being the same number having axes parallel to one medial line as to any other.

Moreover, each so-called (1 1 1) plane, one that is perpendicular to one of the diagonals of the cube, must have the axes of its atoms arranged as shown in fig. 2, p. 259 of the August 1915 paper referred to, which is also re-drawn

Fig. 1 A.

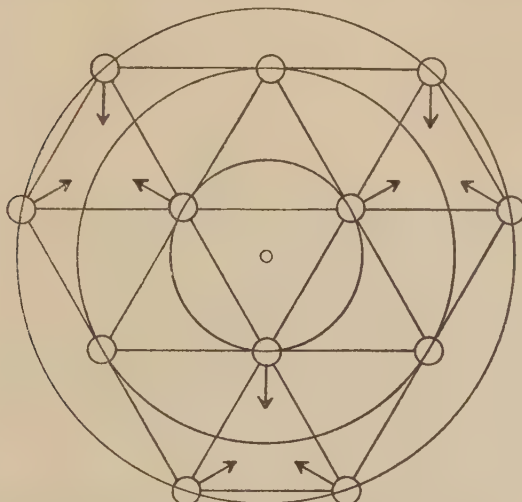


Showing the directions of the axes of the atoms in plane No. 0 of the simple cubic lattice. The small circles without arrows represent atoms with axes pointing upward perpendicular to the paper.

here as figs. 1 A, 1 B, and 1 C. The circles indicate axes pointing upward perpendicular to the plane of the paper, while the arrows represent axes pointing downward but projected on to the paper. These latter make an angle whose cosine is 1/3 with the downward perpendicular, or of $-1/3$ with the upward perpendicular, that is to say with the axes of the atoms shown as plain circles. The cosine of the angle between any two axes or arrows in different

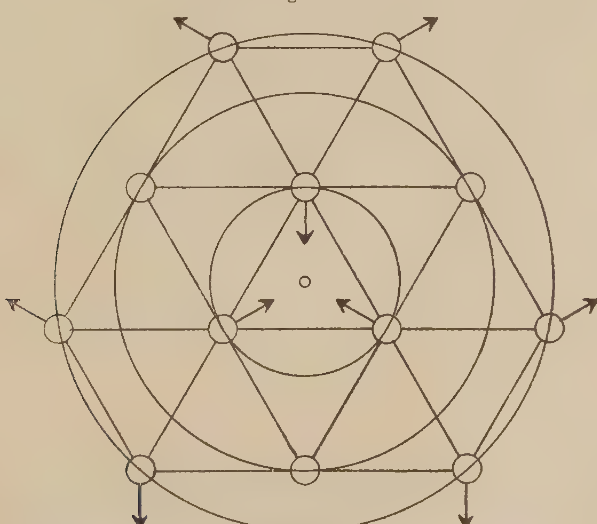
groups is then $-1/3$, so that $\alpha = 109° \ 28'{\cdot}3$, the angle between any two medial lines of a regular tetrahedron.

Fig. 1 B.



Showing the directions of the axes of the atoms in plane No. 1 of the simple cubic lattice.

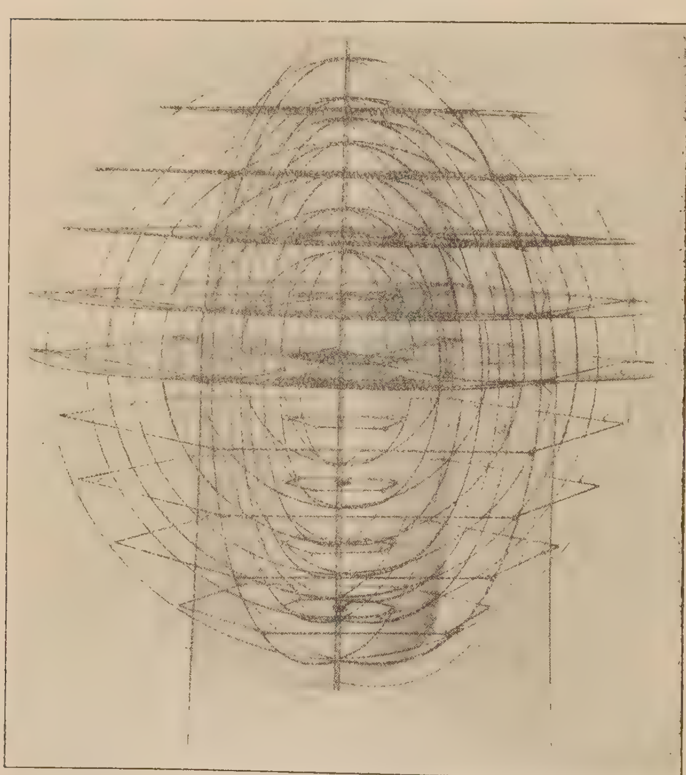
Fig. 1 C.



Showing the directions of the axes of the atoms in plane No. 2 of the simple cubic lattice.

In each of the four forms of cubic lattice above enumerated each (1 1 1) plane is in all respects like fig. 1 A and like every other such plane. Consecutive planes cannot, however, always be brought into coincidence merely by moving the whole plane parallel to the cube diagonal. They must sometimes be shifted laterally, because the points of the equilateral triangles will sometimes fall upon the centres of those in a different plane.

Fig. 2 A.

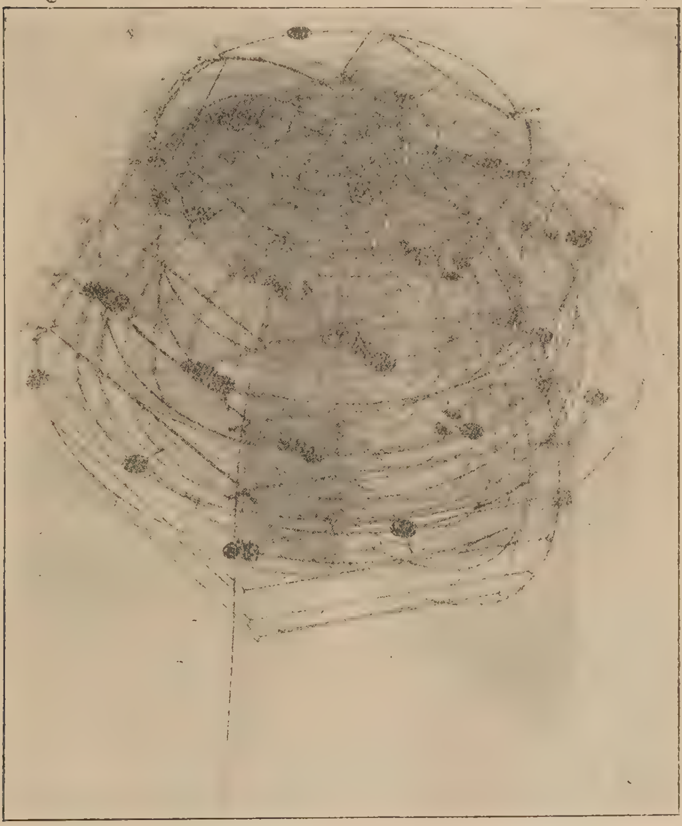


A side view of the model of the simple cubic lattice showing seven concentric spheres of atoms.

To represent all this in a model lattice requires more than is included in the models of lattices as at present constructed. A photographic reproduction of a model of a simple cubic lattice is shown in two different views in figs. 2 A and 2 B. It is made of sheets of transparent celluloid on which black

dots are drawn to indicate the atoms at the points of the lattice. Six vertical sheets set at 60° apart support the parallel (1 1 1) planes, which are equidistant, their separation being 1/3 the diagonal of the elementary cube, or $\frac{1}{3}\sqrt{3}$ times the cube edge.

Fig. 2 B.



View of the model of the simple cubic lattice from a point which shows the elementary cubes.

About any selected atom of the lattice the neighbouring atoms are all arranged in several concentric spheres of increasing radii. Seven of these concentric spheres are contained in the model, their intersections with the six vertical planes being clearly shown by the seven concentric circles drawn on each vertical plane. The horizontal plane

through the selected atom at the centre of the spheres is the No. 0 plane, the first plane above it No. 1, the next No. 2, and so on. The top plane in the model is No. 4 containing atoms belonging to the 6th and 7th spheres only. The 5th sphere does not intersect this plane. Planes below the zero plane are numbered -1, -2, etc., but these have been omitted from the model. Each negative plane is, however, the counterpart of the positive plane with the corresponding number, being symmetrical with respect to the centre of the sphere, the directions of the axes at corresponding points being parallel to each other. The planes numbered 0, 1, and 2 of the model are shown as figs. 1 A, 1 B, and 1 C above referred to.

TABLE I.

Cubic Lattice.

Plane 0. See fig. 1 A. $z=0$.

No. Sphere.	No. Circle.	No. Atoms.	$\cos\alpha$.	$r'^2=r^2$.	$r'=r$.
0	0	1	1	0	0
2	1	6	$-1/3$	$2\,l^2$	$\sqrt{2}\,l = 1{\cdot}41421$
6	2	6	$-1/3$	6 „	$\sqrt{6}$ „ $= 2{\cdot}44949$ „
7	3	6	1	8 „	$2\sqrt{2}$ „ $= 2{\cdot}82842$ „
13	4	12	$-1/3$	14 „	$\sqrt{14}$ „ $= 3{\cdot}7417$ „
16	5	6	$-1/3$	18 „	$3\sqrt{2}$ „ $= 4{\cdot}2426$ „
21	6	6	1	24 „	$2\sqrt{6}$ „ $= 4{\cdot}8990$ „
23	7	12	$-1/3$	26 „	$\sqrt{26}$ „ $= 5{\cdot}0990$ „
	8	6	1	32 „	$4\sqrt{2}$ „ $= 5{\cdot}6569$ „
	9	12	$-1/3$	38 „	$\sqrt{38}$ „ $= 6{\cdot}1644$ „

r' = radius circle. r = radius sphere. l = cube edge.

In Table I. the second column gives the number of the circle in the zero plane including nine consecutive concentric circles, the third column gives the number of atoms in each circle, the fourth column the value of $\cos\alpha$, which

gives the angle that the axis of the given atom makes with the selected atom at the origin. Each atom in any one circle has the same value of $\cos\alpha$. The fifth column gives the square of the radius of the circle in terms of l, the edge of the elementary cube of the lattice as a unit, while the last column gives the radius itself.

Now there are certain spheres of atoms in the cubic lattice that include atoms occurring in the odd planes only, and that do not include any in the zero plane, and again there are spheres with atoms in other even planes that do not include any in the zero plane. Consequently the number of the sphere given in the first column counting from the smallest outwards increases faster than the number of the circle in the zero plane. The radius of the sphere is found from the radius of the circle by the formula

$$r^2 = r'^2 + z^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where r is the sphere's and r' the circle's radius, and z is the distance of the plane in question from the zero plane. For the zero plane, where $z=0$, the radii of sphere and circle are the same as shown in the last column of the Table. These radii in planes 0, 3, 6, etc. are computed from a centre at the point of one of the fundamental equilateral triangles in the plane, namely the selected atom ; but in planes 1 and 2 the radii have to be computed from a centre at the centre of one of these fundamental triangles, instead of from its apex.

Table II. gives for plane 1 the data corresponding to that of Table I. Here, however, the radius of the sphere is greater than that of the corresponding circle because z is no longer zero. It may be remarked that $\cos\alpha$ is the same for each atom in any one circle as before. No Table for plane 2 and other planes is required, because the radii of the circles in the plane as well as the values of $\cos\alpha$ are the same for a circle of the same number as given in Table II. The sphere's radius must be computed, however, by the use of (1).

The cubic lattice is described with some completeness in Table III., including ten concentric spheres. The smallest sphere, No. 1, has a radius, l, equal to the cube edge and given in the second column. The angle, α, is designated by the value of $\cos\alpha$ in the third column. It has the value $+1$ or $-1/3$ in every case. Then follow in columns 4, 5, 6, and 7 the number of the (1 1 1) plane, the number of the circle in that plane, the number of atoms in that circle

and plane belonging to the sphere in question, and in column 7 the total number of atoms in that sphere.

TABLE II.

Cubic Lattice.

PLANE 1. See fig. 1 B. $z=(\sqrt{3}/3)l$; $z^2=(1/3)l^2$.

No. Sphere.	No. Circle.	No. Atoms.	cos α.	r'^2.	r^2.	r.
1	1	3	-1/3	$(2/3)\ l^2$	l^2	$l = 1{\cdot}00000\ l$
3	2	3	1	„ 4 „	3 „	$\sqrt{3}$ „ = 1·73205 „
5	3	6	−1/3	„ 7 „	5 „	$\sqrt{5}$ „ = 2·23607 „
8	4	6	−1/3	„ 13 „	9 „	3 „ = 3·00000 „
10	5	3	1	„ 16 „	11 „	$\sqrt{11}$ „ = 3·3166 „
12	6	6	−1/3	„ 19 „	13 „	$\sqrt{13}$ „ = 3·6056 „
15	7	3	−1/3	„ 25 „	17 „	$\sqrt{17}$ „ = 4·1231 „
17	8	6	1	„ 28 „	19 „	$\sqrt{19}$ „ = 4·3589 „
19	9	6	−1/3	„ 31 „	21 „	$\sqrt{21}$ „ = 4·5826 „
22	10	6	−1/3	„ 37 „	25 „	5 „ = 5·0000 „
	11	6	−1/3	„ 43 „	29 „	$\sqrt{29}$ „ = 5·3852 „
	12	9	−1/3	„ 49 „	33 „	$\sqrt{33}$ „ = 5·7446 „
	13	6	1	„ 52 „	35 „	$\sqrt{35}$ „ = 5·9161 „

$$r^2 = r'^2 + z^2.$$

The direction cosines X, Y, and Z are given in columns 8, 9, and 10, defining the position of the second atom with respect to the selected atom in terms of the i, j, and k axes. Where a double sign is given, as for example in sphere 8, plane 3, circle 2, $X = \pm\frac{1}{3}\sqrt{6}$, the meaning is that of the six atoms in this circle three of them, or one half of them, have the positive and three have the negative sign. Where no double sign is indicated, each atom in the respective circle has the same direction cosine. But it should be

stated here that because of the manner in which the expressions for the forces have been derived the xi- and yj-axes each take three different positions in the horizontal (1 1 1) plane at angles of 120° apart, while the zk-axis alone remains fixed, being perpendicular to this plane. This is due to the fact that the direction of the yj-axis is defined by the vector $k \times k'$, where k is a unit vector along the axis of the selected atom and k' a unit vector along the axis of the given atom. The directions of the x and y axes are immaterial in getting the zk-component of the force. But the zk-component is the whole force because the xi- and yj-components evidently vanish for each and every circle in the lattice. In each case the sum of these forces for one circle of atoms gives three equal forces in the x, y plane at angles of 120° apart. These give a sum equal to zero. The zk-component is, therefore, the total force, and moreover, the axis of the atom always sets itself in the direction of this total force.

Column 11 of Table III. gives the product XZ, and column 12 the sum of these products for the sphere; while the last column gives the total number of atoms including all spheres. It will be shown that this product XZ is required for the purpose of summing the z-forces for the whole cubic lattice. We shall now make use of the expression for the force upon the positive charge of a first atom due to the whole of a single second atom situated in any position. The derivation of these expressions is given in a separate communication, so that some applications may be discussed here without unnecessary interruption. It has been proven that the force upon the positive charge of a hydrogen atom at the origin of coordinates due to the whole of a second hydrogen atom in any position is given by an infinite series of terms in r^{-3}, r^{-4}, etc., r being the distance between the centres of the atoms. The first term of the series is the r^{-3} term, and the whole force is given to a very close approximation indeed by the first two terms only of the series. The first term of this series is as follows:

$$F_z = \frac{e^2}{k}\{2(-3Z\zeta + \cos\alpha)Dr^{-3}\}, \quad . \quad . \quad . \quad . \quad (2)$$

where ζ stands for

$$\zeta = Z\cos\alpha - X\sin\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and D for the quantity $b_2 - b_1$ discussed in the last paper, b_2 being the semi-minor axis of the upper electron and b_1 that of the lower electron of the hydrogen atom.

Table III.—Cubic Lattice.

No. Sphere.	Radius sphere.	Cos a.	No. Plane.	No. Circle.	Atoms in circle.	Atoms in sphere.	X.	Y.	Z.	XZ.	Σ XZ (Sphere).	Total No. Atoms.
1	l	$-\frac{1}{3}$	1	1	3	6	$\frac{1}{3}\sqrt{6}$	0	$\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{2}$	$2\sqrt{2}$	
	$p^{-3}=1$. $\Sigma(-3Z\zeta+\cos a)p^{-3}=3\sin ap^{-3}\,\Sigma XZ=+8$.											6
2	$\sqrt{2}\,l$	$-\frac{1}{3}$	0	1	6		0	± 1	0	0		
	,,	,,	2	1	3	12	$-\frac{1}{3}\sqrt{3}$	0	$\frac{1}{3}\sqrt{6}$	$-\frac{1}{3}\sqrt{2}$	$-2\sqrt{2}$	
	$p^{-3}=\frac{1}{4}\sqrt{2}$. Σ (for sphere) $=-2\sqrt{2}$; Σ (total) $=+5{\cdot}17158$.											18
3	$\sqrt{3}\,l$	1	1	2	3		$\frac{2}{3}\sqrt{2}$	0	$\frac{1}{3}$			
	,,	,,	3	0	1	8	0	0	1			
	$p^{-3}=\frac{1}{9}\sqrt{3}$. Σ (for sphere) $=0$; Σ (total) $=+5{\cdot}17158$.											26
4	$2\,l$	1	2	2	3	6	$\frac{1}{3}\sqrt{6}$	0	$\frac{1}{3}\sqrt{3}$			
	$p^{-3}=\frac{1}{8}$. Σ (for sphere) $=0$; Σ (total) $=+5{\cdot}17158$.											32
5	$\sqrt{5}\,l$	$-\frac{1}{3}$	1	3	6		$-\frac{2}{15}\sqrt{30}$	$\pm\frac{1}{5}\sqrt{10}$	$\frac{1}{15}\sqrt{15}$	$-\frac{2}{15}\sqrt{2}$		
	,,	,,	3	1	6	24	0			0	$-\frac{8}{5}\sqrt{2}$	
	$p^{-3}=\frac{1}{25}\sqrt{5}$. Σ (for sphere) $=-\frac{32\sqrt{5}}{125}$; Σ (total) $=+4{\cdot}59915$.											56

6	$\sqrt{6}\,l$	$-\frac{1}{3}$	0	2	6		± 1	0	0	0		
	,,	,,	2	3	6		$\frac{2}{3}$	$\frac{1}{3}\sqrt{3}$	$\frac{1}{3}\sqrt{2}$	$\frac{2}{9}\sqrt{2}$		
	,,	,,	4	1	3	24	$\frac{1}{3}$	0	$\frac{2}{3}\sqrt{2}$	$\frac{2}{9}\sqrt{2}$	$4\sqrt{2}$	
	$p^{-3}=\frac{1}{36}\sqrt{6}$. Σ (for sphere) $=\frac{4}{9}\sqrt{6}$; Σ (total) $=+5{\cdot}68781$.											80
7	$2\sqrt{2}\,l$	1	0	3	6		1	0	0	0		
	,,	,,	4	2	3	12	$\frac{1}{3}\sqrt{3}$	0	$\frac{1}{3}\sqrt{6}$			
	$p^{-3}=\frac{1}{32}\sqrt{2}$. Σ (for sphere) $=0$; Σ (total) $=+5{\cdot}68781$.											92
8	$3\,l$	$-\frac{1}{3}$	1	4	6		$\frac{1}{9}\sqrt{6}$	$\frac{2}{3}\sqrt{2}$	$\frac{1}{9}\sqrt{3}$	$\frac{1}{27}\sqrt{2}$		
	,,	,,	3	2	6		$\pm\frac{1}{3}\sqrt{6}$	0	$\frac{1}{3}\sqrt{3}$	$\pm\frac{1}{3}\sqrt{2}$		
	,,	,,	5	1	3	30	$-\frac{1}{9}\sqrt{6}$	0	$\frac{5}{9}\sqrt{3}$	$-\frac{5}{27}\sqrt{2}$	$-\frac{2}{3}\sqrt{2}$	
	$p^{-3}=\frac{1}{27}$. Σ (for sphere) $=-\frac{8}{81}$; Σ (total) $=+4{\cdot}70015$.											122
9	$\sqrt{10}\,l$	$-\frac{1}{3}$	2	4	6		$-\frac{1}{15}\sqrt{15}$	$\pm\frac{2}{5}\sqrt{5}$	$\frac{1}{15}\sqrt{30}$	$-\frac{1}{15}\sqrt{2}$		
	,,	,,	4	3	6	24	$-\frac{2}{15}\sqrt{15}$	$\pm\frac{1}{5}\sqrt{5}$	$\frac{2}{15}\sqrt{30}$	$-\frac{4}{15}\sqrt{2}$	$-4\sqrt{2}$	
	$p^{-3}=\frac{1}{100}\sqrt{10}$. Σ (for sphere) $=-\frac{4}{25}\sqrt{10}$; Σ (total) $=+4{\cdot}1042$.											146
10	$\sqrt{11}\,l$	1	1	5	3							
	,,	,,	3	3	6							
	,,	,,	5	2	3	24						
	$p^{-3}=\frac{1}{121}\sqrt{11}$. Σ (for sphere) $=0$; Σ (total) $=+4{\cdot}1042$.											170

The use of the word upper means that electron on the positive side of the k or k' axes respectively. Eliminating ζ between (2) and (3) gives as the equivalent of (2)

$$F_z = \frac{e^2}{k}\{2\cos\alpha(1-3Z^2)+6XZ\sin\alpha\}(b_2-b_1)r^{-3}. \quad (4)$$

Before proceeding to sum this expression for the whole cubic lattice, there are several points shown by Table III. which may be noted :—

1. The points of the cubic lattice, at each of which one atom is located, in any one sphere about any selected atom either lie all in the even or in the odd planes, but never in both even and odd.
2. The angle alpha is the same for each atom in any one sphere, $\cos\alpha$ being either $-1/3$ or $+1$ for any given sphere.
3. The sum of the quantity $(1-3Z^2)$ taken for all the atoms in each and every sphere is zero, and consequently this sum is zero for the whole cubic lattice.
4. In those spheres where $\cos\alpha=1$, the axes of the atoms being parallel to that of the selected atom, $\sin\alpha=0$. Therefore the second term of (4) vanishes for all such spheres, and because the first term of (4) also vanishes for all such spheres because of the statement in 3 above, it follows that the sum of the expressions (4) vanishes for all spheres in the cubic lattice having parallel axes.

Table III. also gives the sum of the quantity that occurs in equation (2), namely $(-3Z\zeta+\cos\alpha)p^{-3}$, for each individual concentric sphere of the cubic lattice as well as the total sum for all the spheres included in the Table. Since r is different for different spheres it is put equal to pl so that the cube edge, which is a constant, may be factored out in taking the sum. Then p is defined as $p=r/l$, and p^{-3} is also given for each sphere.

Table IV. is an extension of Table III. to include thirty concentric spheres. To economize space the direction cosines have been omitted, but by the guidance of Table III. the reader will be able to supply them if desired to check the results in Table IV.

By writing

$$S = \Sigma(-3Z\zeta+\cos\alpha)\,p^{-3}, \quad . \quad . \quad . \quad (5)$$

the summation being supposed to be extended over the

TABLE IV.

Cubic Lattice.

No. Sphere.	Radius sphere.	cos a.	Atoms in sphere.	Atoms, total.	$\Sigma(-3Z\zeta+\cos a)p^{-3}$. For sphere. +	$\Sigma(-3Z\zeta+\cos a)p^{-3}$. For sphere. −	Total for Cubic Lattice.
1	l	$-\frac{1}{3}$	6	6	8·0000		+8·00000
2	$\sqrt{2}$,,	,,	12	18		2·82842	5·17158
3	$\sqrt{3}$,,	1	8	26	0		,,
4	2 ,,	1	6	32	0		,,
5	$\sqrt{5}$,,	$-\frac{1}{3}$	24	56		0·57243	4·59915
6	$\sqrt{6}$,,	,,	24	80	1·08866		5·68781
7	$2\sqrt{2}$,,	1	12	92	0		,,
8	3 ,,	$-\frac{1}{3}$	30	122		0·98765	4·70016
9	$\sqrt{10}$,,	,,	24	146		0·50597	4·19419
10	$\sqrt{11}$,,	1	24	170	0		,,
11	$2\sqrt{3}$,,	1	8	178	0		,,
12	$\sqrt{13}$,,	$-\frac{1}{3}$	24	202	0·36762		4·56180
13	$\sqrt{14}$,,	$-\frac{1}{3}$	48	250		0·087270	4·47453
14	4 ,,	1	6	256	0		,,
15	$\sqrt{17}$,,	$-\frac{1}{3}$	48	304		0·093993	4·38054
16	$3\sqrt{2}$,,	$-\frac{1}{3}$	36	340	0·244431		4·62497
17	$\sqrt{19}$,,	1	24	364	0		,,
18	$2\sqrt{5}$,,	1	24	388	0		,,
19	$\sqrt{21}$,,	$-\frac{1}{3}$	48	436		0·285021	4·33995
20	$\sqrt{22}$,,	,,	24	460		0·070479	4·26947
21	$2\sqrt{6}$,,	1	24	484	0		,,
22	5 ,,	$-\frac{1}{3}$	30	514	0·074240		4·34371
23	$\sqrt{26}$,,	,,	72	586	0·083552		4·42726
24	$3\sqrt{3}$,,	1	32	618	0		,,
25	$\sqrt{29}$,,	$-\frac{1}{3}$	72	690	0 14838		4·57564
26	$\sqrt{30}$,,	,,	48	738		0·084389	4·49125
27	$4\sqrt{2}$,,	1	12	750	0		,,
28	$\sqrt{33}$,,	$-\frac{1}{3}$	36	786	0·030664		4·52192
29	$\sqrt{34}$,,	,,	48	834		0·047474	4·47444
30	$\sqrt{35}$,,	1	48	882	0		,,

whole of an infinite cubic lattice, it follows from (2) for the r^{-3} term only of the force that

$$F_z = \frac{e^2}{k}(2SD)l^{-3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

since the displacement, D, must be the same for every atom. Including 30 concentric spheres comprising 882 atoms, Table IV. shows that the approximate value of S is

$$S = 4{\cdot}474. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

An inspection of the last column of the Table shows the rapidity with which this summation approaches a limit for a larger number of spheres. For a very accurate value of S undoubtedly more spheres than 30 should be included. The radius of the thirtieth sphere is 5·9161 times the cube edge. The reason that these outlying spheres have any effect is the low order of the term, the inverse third power of the distance. The higher the order of the term the less spheres need be included. It follows from (6) and (7) that the sum of the forces of the whole lattice upon the positive charge of the selected hydrogen atom, so far as the r^{-3} atom is concerned and provided that hydrogen can form a simple cubic crystal in a stable form, is

$$F_z = \frac{e^2}{k}(8{\cdot}949)\,Dl^{-3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It will now be shown that (8) very approximately represents the whole force of the lattice upon the positive charge of one hydrogen atom, that is each hydrogen atom. This is because the r^{-4} term of the force-series vanishes for a cubic lattice and the higher order terms are small and negligible in any case. The complete expression for the force of a second hydrogen atom upon the positive charge of a first hydrogen atom including the r^{-4} term is, instead of (2), as follows:

$$F_z = \frac{e^2}{k}\{2f_1 Dr^{-3} + 3f_2(2b^2 - \rho a^2)r^{-4} \ldots\}, \quad . \quad . \quad (9)$$

where f_1 and f_2 denote functions of X, Y, Z, and α as follows:

$$f_1 = -3Z\zeta + \cos\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$f_2 = 5Z\zeta^2 - Z - 2\zeta\cos\alpha, \quad . \quad . \quad . \quad (11)$$

where ζ is given by (3).

For any lattice that is symmetrical with respect to a

centre, like the simple cubic lattice, and in which the atoms at each pair of corresponding points have parallel axes, as they have in the lattice described, the direction cosines are each reversed in sign for the second atom of such a pair. Now the function of X, Y, and Z in the r^{-4} term of (9), namely (11), contains them only in an odd degree, and therefore the whole function merely changes sign for each pair of such atoms and cancels out completely in taking the sum for each pair and so for the whole lattice. This leaves the expression (8) as representing the whole force very approximately.

In the last communication the effect of the comparatively large internal forces acting within an atom in opposite directions upon positive and negative charges was discussed in some detail. For the hydrogen atom there are two constants, ρ_x and ρ_z, the former proportional to the lateral or equatorial displacement of the positive charge off from the centre line of the two electrons, and the latter to this quantity $D = b_2 - b_1$, which occurs in (8). The numerical value of ρ_z was determined in that paper to be $30{\cdot}7 \times 10^{24}$ derived from the property of the negative electron itself. In the present instance the equatorial force upon the positive charge of the atom is zero as above stated because of the property of the lattice, so that we do not require the constant, ρ_x. The force upon the positive charge in the axial direction is proportional to D and equal to

$$F_z = \frac{e^2}{k}(-\rho_z D) = -\frac{e^2}{k}(30{\cdot}7 \times 10^{24})D. \quad . \quad . \quad (12)$$

The reason for the negative sign given in the paper referred to should perhaps be repeated here. The force upon the positive charge is to be regarded as the cause of the displacement, D, so that it vanishes when the force vanishes, being proportional to the force for small displacements as they always are. Now b_2 denotes the semi-minor axis of the electron on the upper side, that is on the positive side of the zk-axis. If this electron has a larger minor axis than that of the lower electron, then D is a positive quantity. But it requires a negative force upon the positive charge, a downward force, and of course a positive force upon each electron to cause the compression of the lower and the expansion of the upper electron. That is to say, (12) requires the negative sign because the force is negative when D is positive, the constant, ρ_z, being essentially a positive quantity.

The First Condition to be Satisfied by a Lattice.

From this it becomes evident that the sign of equation (8), the total force of the lattice upon the positive charge, is wrong if it is to satisfy the required conditions for a stable cubic lattice. If D is positive this force is also positive, and a positive force cannot give rise to a positive value of D. Equations (8) and (12) should be expressions for the same force, but it is absurd to equate them because of the different signs. This constitutes a proof that the simple cubic lattice for hydrogen is not a possibility. By equating them we obtain a negative value for l, the cube edge, which is absurd. Overlooking, however, this absurdity for the moment, it is of some interest to note that the method in general does give a numerical value for l, even if absurd in this instance. We have

$$\frac{e^2}{k}(8{\cdot}949)\mathrm{D}l^{-3} = -\frac{e^2}{k}(30{\cdot}7 \times 10^{24})\mathrm{D}, \quad . \quad . \quad . \quad (13)$$

whence $$l^{-3} = -3{\cdot}43 \times 10^{24} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and $$l = -0{\cdot}663 \times 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad (15)$$

The legitimate conclusion is that hydrogen does not crystallize in the form of a simple cubic lattice, which has been used as a basis for equation (8). The writer is not aware that any of the so-called chemical elements crystallizes in the form of a simple cubic lattice. It seems to require at least two different kinds of atoms to form such a lattice, as for example sodium chloride, potassium chloride, or potassium iodide. In such crystals alternate (1 1 1) planes contain different kinds of atoms, and this gives a different resulting sum for the forces. It is now believed that this result, although worked out above on the basis of hydrogen alone, will prove to be true for the atoms of any other single element, and this investigation offers the reason why simple cubic crystals for the elements alone do not occur. This has been substantiated in the specific case of the carbon atom to be described below, and it is considered to be a general result. It is in complete agreement with experimental observations on crystals.

The Face-centred Cubic Lattice.

The next form of lattice to be treated is that of the so-called face-centred cubic lattice. A careful study of this lattice shows that the complete data for it may be

obtained directly from that of the simple cubic lattice above given. There are several points that will be noticed.

1. The (1 1 1) planes perpendicular to a cube diagonal are equally spaced at a distance of 1/3 the cube diagonal, namely $\frac{1}{3}\sqrt{3}\,l$, and in fact are spaced the same as the corresponding planes of the simple cubic lattice.

2. The edge of the elementary equilateral triangle, however, in each plane is one half as long as that of the triangle in the simple cubic lattice. In the cubic it is $\sqrt{2}l$ and in the face-centred cubic $\frac{1}{2}\sqrt{2}l$.

3. Because of this difference in the size of the equilateral triangles the arrangement of the axes of the atoms in the corresponding (1 1 1) planes is also different. The zero plane in each lattice may be represented by fig. 1 A. In the simple lattice plane No. 1 must be like fig. 1 B, where the arrows of the central triangle point outward, and plane No. 2 like fig. 1 C, where they point inward, whereas in the face-centred lattice plane No. 1 must be like fig. 1 C, the arrows of the inner circle pointing inward, because this inner triangle forms a regular tetrahedron with the selected atom at the origin and all arrows point toward the centre of this tetrahedron. In a similar manner the inner triangle of plane No. 2 of the simple cubic forms a regular tetrahedron with the atom at the origin, but of twice the length of side, and all arrows point towards its centre.

4. Table V. gives the numbers of the planes in the cubic and face-centred lattices respectively that are arranged according to the three figures, 1 A, 1 B, and 1 C.

Table V.

	Like fig. 1 A.	Like fig. 1 B.		Like fig. 1 C.	
	Cubic or Face-centred.	Cubic.	Face-centred.	Cubic.	Face-centred.
	......	......	......	......	......
No. plane.	9	7	8	8	7
	6	4	5	5	4
	3	1	2	2	1
	0	−2	−1	−1	−2
	3	−5	−4	−4	−5
	6	−8	−7	−7	−8
	......	......	......	......	......

5. Table VI. follows immediately from the correspondences in Table V. The numbers of the planes set opposite to each other in Table VI. are those in which the atoms are located in an identical manner including the directions of their axes.

TABLE VI.

No. plane.	Face-centred Lattice.	Simple Cubic Lattice.
	8	16
	7	14
	6	12
	5	10
	4	8
	3	6
	2	4
	1	2
	0	0

6. It follows from Table VI. that a face-centred lattice may be formed from a simple cubic lattice merely by omitting all of the odd planes of the cubic lattice, and then reducing the dimensions of the lattice by a factor of 2, because the edge of the equilateral triangle of the cubic is twice that of the face-centred lattice. Consequently the same computations made above for the simple cubic may now be used for the face-centred lattice, provided we substitute $\frac{1}{2}l$ for l. In the r^{-3} term of the force-equation this makes l^{-3} eight times its former value.

7. By consulting Tables III. and IV. for the simple cubic lattice it will appear that when all of the odd planes are omitted the numbers of the concentric spheres that remain are given by the upper row of figures in Table VII. These spheres alone therefore constitute a face-centred lattice, some spheres having even and some odd numbers. The spheres may then be renumbered consecutively as in the lower row of figures. Sphere No. 10, for example, of the face-centred lattice is identical in all respects with sphere No. 18 of the simple cubic lattice when its dimensions are divided by 2.

TABLE VII.

Numbers of Spheres.

Cubic	2,	4,	6,	7,	9,	11,	13,	14,	16,	18,	20,	21,	23,	26,	27,	29.
Face-centred ...	1,	2,	3,	4,	5,	6,	7,	8,	9,	10,	11,	12,	13,	14,	15,	16.

8. It is no longer true, however, that each sphere of the face-centred lattice embraces atoms either in odd or even planes, as was the case with the cubic lattice. This is because some of the even planes of the cubic receive an odd number in the face-centred lattice. The numbers of the spheres of the face-centred lattice that contain atoms in even, odd, or even and odd planes is given in Table VIII.

Table VIII.

	Even planes.	Odd planes.	Even and Odd planes.	
Sphere numbers, Face-centred Cubic Lattice.	4	1	3	11
	8	2	5	13
	12	6	7	14
	15	10	9	16

9. It still holds true, however, that $\cos\alpha$ has the same value for each atom in any one sphere, being either $-1/3$ or $+1$.

10. The face-centred lattice is also symmetrical about the centre, that is to say about any selected atom. Each atom is matched by another at the same distance on the opposite side of the centre, having its axis parallel to that of the given atom. The direction cosines X, Y, and Z are each reversed in sign for the second atom of such a pair.

11. It follows from the statement in 10 that the sum of the r^{-4} terms of the force equation (9) will vanish for the face-centred lattice as they did for the cubic lattice, because the direction cosines occur in odd degrees only.

12. The sum of the forces according to (2) or (9) may, therefore, be found for the whole face-centred lattice by the use of Table IV. compiled for the simple cubic lattice by picking out those spheres only that form the face-centred lattice according to Table VII., and multiplying each sum by 8 for the reason above stated. This result is given in Table IX. The numbers given are, however, the same as for the cubic lattice in Table IV., the final result only being multiplied by 8 instead of the individual sums for each sphere.

For a face-centred cubic lattice, therefore, comprising 16 spheres embracing 428 atoms, we find

$$S = \Sigma(-3Z\zeta + \cos a)p^{-3} = -17{\cdot}659. \quad . \quad . \quad (16)$$

And according to (2) or (9) the whole force upon the positive charge of the single hydrogen atom at the centre is

$$F_z = \frac{e^2}{k}(-35{\cdot}32)Dl^{-3}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

TABLE IX.

Face-centred Cubic Lattice.

No. Sphere.	Radius sphere.	cos a.	Atoms in sphere.	Atoms, total.	$\frac{1}{8}\Sigma(-3Z\zeta+\cos a)p^{-3}$. For sphere. +	$\frac{1}{8}\Sigma(-3Z\zeta+\cos a)p^{-3}$. For sphere. −	Total for face-centred cubic lattice.
1	$\frac{1}{2}\sqrt{2}\ l$	$-\frac{1}{3}$	12	12		2·82842	−2·82842
2	1 ,,	1	6	18	0		,,
3	$\frac{1}{2}\sqrt{6}$,,	$-\frac{1}{3}$	24	42	1·08866		−1·30976
4	$\sqrt{2}$,,	1	12	54	0		,,
5	$\frac{1}{2}\sqrt{10}$,,	$-\frac{1}{3}$	24	78		0·50597	−2·24573
6	$\sqrt{3}$,,	1	8	86	0		,,
7	$\frac{1}{2}\sqrt{14}$,,	$-\frac{1}{3}$	48	134		0·087070	−2·33300
8	2 ,,	1	6	140	0		,,
9	$\frac{3}{2}\sqrt{2}$,,	$-\frac{1}{3}$	36	176	0·244431		−2·08857
10	$\sqrt{5}$,,	1	24	200	0		,,
11	$\frac{1}{2}\sqrt{22}$,,	$-\frac{1}{3}$	24	224		0·070479	−2·15905
12	$\sqrt{6}$,,	1	24	248	0		,,
13	$\frac{1}{2}\sqrt{26}$,,	$-\frac{1}{3}$	72	320	0·083552		−2·07550
14	$\frac{1}{2}\sqrt{30}$,,	$-\frac{1}{3}$	48	368		0·084389	−2·15989
15	$2\sqrt{2}$,,	1	12	380	0		,,
16	$\frac{1}{2}\sqrt{34}$,,	$-\frac{1}{3}$	48	428		0·047474	−2·20736

$$\Sigma(-3Z\zeta+\cos a)p^{-3}=-17\cdot659.$$

Comparing this result with (8) for the simple cubic lattice it appears that the sign has changed and that the value is more than four times larger. As pointed out above, it is necessary that the sign be negative to satisfy the requirements. The simple cubic lattice would not answer for a single element because of the sign being wrong. As

before, we may now equate this new expression in (17) to (12) and find

$$-35{\cdot}32\,\mathrm{D}l^{-3}=-30{\cdot}7\times10^{24}\,\mathrm{D}, \quad . \quad . \quad . \quad . \quad (18)$$

from which D cancels giving

$$l^{-3}=0{\cdot}87\times10^{24}\,; \quad l=1{\cdot}05\times10^{-8}\text{ cm.} \quad . \quad . \quad (19)$$

This result admits of the possibility that hydrogen may form face-centred cubic crystals, but it is by no means conclusive. The test has now advanced one step further than before without meeting with any obstacle. We might now turn to the experimental evidence contained in the density of solid hydrogen to see whether such a small value of the cube edge as found in (19) can possibly satisfy this density, but it seems a better plan to examine the second theoretical requirement to ascertain whether it too is satisfied.

The Second Condition to be Satisfied by the Lattice.

A second theoretical requirement that must be satisfied by any form of lattice is that the total force upon each and every atom in it shall be equal to zero in the condition of stable equilibrium. This involves a second equation which may next be given, the derivation of it being reserved for another paper. The total force of a second hydrogen atom in the position X, Y, Z, r, and α upon a first hydrogen atom at the origin with axis along the zk-axis is as follows :—

$$\underset{\mathrm{H}_2\text{ on }\mathrm{H}_1}{\mathrm{F}_z}=\frac{3e^2}{k}\{f_3\mathrm{D}^2r^{-4}$$
$$+[f_4b^2\mathrm{D}-\tfrac{1}{2}(f_5+f_6)\rho a^2\mathrm{D}]r^{-5}$$
$$+[5f_7b^4+\tfrac{5}{2}(f_8+2f_9)\rho a^2b^2-\tfrac{5}{2}f_{10}\rho^2a^4]r^{-6}\}, \quad (20)$$

where f_3 to f_{10} are functions of X, Y, Z, and α as follows :—

$$f_3=5\mathrm{Z}^2\zeta-3\mathrm{Z}\cos\alpha+\mathrm{X}\sin\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$f_4=\cos\alpha(1-\cos\alpha)(3-30\mathrm{Z}^2+35\mathrm{Z}^4)$$
$$+10\sin\alpha(\tfrac{1}{2}-\cos\alpha)\mathrm{XZ}(3-7\mathrm{Z}^2)$$
$$+\sin^2\alpha[5(\mathrm{X}^2+\mathrm{Z}^2)-35\mathrm{X}^2\mathrm{Z}^2-1], \quad . \quad (22)$$

$$f_5=5\mathrm{XZ}(3-7\mathrm{Z}^2)\sin\alpha$$
$$+(3-30\mathrm{Z}^2+35\mathrm{Z}^4)\cos\alpha, \quad . \quad . \quad . \quad . \quad (23)$$

$$f_6=2-10\mathrm{Z}^2-5\mathrm{Y}^2+35\mathrm{Z}^2(\xi^2+\mathrm{Y}^2)$$
$$-10\mathrm{Z}\xi\sin\alpha-20\mathrm{XZ}\sin\alpha\cos\alpha$$
$$+(2-15\mathrm{Z}^2)\sin^2\alpha-5\mathrm{X}^2\cos^2\alpha, \quad . \quad . \quad (24)$$

$$* f_7 = -63Z^3\zeta^2 + Z(21X^2 - 7Z^2 - 3)\sin^2\alpha$$
$$+ Z(70Z^2 - 15)\cos^2\alpha$$
$$+ X(6 - 84Z^2)\sin\alpha\cos\alpha, \quad . \quad . \qquad (25)$$

$$f_8 = -21Z\zeta^2(1 - 3Z^2) + Z(3 - 7Z^2)$$
$$+ 6\zeta(1 - 7Z^2)\cos\alpha + 6Z\cos^2\alpha, \quad . \quad . \qquad (26)$$

$$f_9 = -(3 - 7Z^2)(Z + \xi\sin\alpha)$$
$$+ 7Z(3Z^2\sin^2\alpha + 4XZ\sin\alpha\cos\alpha + X^2\cos^2\alpha)$$
$$+ \tfrac{7}{2}Z(1 - 9Z^2)(\xi^2 + Y^2), \quad . \quad . \quad . \quad . \quad . \qquad (27)$$

$$f_{10} = 3Z - 7Z(X^2 + 4Y^2 + \xi^2) + \tfrac{63}{2}Z(\xi^2 + Y^2)(X^2 + Y^2)$$
$$+ 2\xi\sin\alpha\left[1 - \tfrac{7}{2}(X^2 + Y^2)\right]$$
$$+ (Z\cos\alpha + 2X\sin\alpha - 14XZ\xi)\cos\alpha, \qquad (28)$$

where $\xi = Z\sin\theta + X\cos\alpha.$

The equation which is equivalent to (20) when the axes of the two hydrogen atoms are parallel to each other has already been published as (100) in the preceding paper †, and it will be found that this reduces to that when we put $\sin\alpha = 0$. The equatorial displacement, l, must also be put equal to zero in that equation in making the comparison, because it is assumed to be zero in (20) above. The equation is there quite fully discussed, and most of the essential points apply also to this more general expression. The striking characteristic is that the series begins with the r^{-4} term and need not include terms beyond the r^{-6} term. The r^{-4} term contains D^2 as a factor, the r^{-5} contains D, while the r^{-6} term contains the fourth degree of a and b, a being the radius of the circle in the circle-and-point electron and b its semi-minor axis. If we make $D = 0$, the r^{-4} and r^{-5} terms vanish and no equilibrium would be possible. It requires the presence of these three terms to fulfil the conditions of an equilibrium.

Let us now consider a single pair of atoms of either the cubic or face-centred lattices at equal distances on opposite sides of the selected atom and having axes parallel to each other. Equal values of f_3 in (21) but with opposite signs are obtained for this pair of atoms because X and Z occur in each term in an odd degree. Hence the sum of these functions for the pair of atoms is zero. It is, therefore, zero for the whole lattice, and the r^{-4} term drops out from the equation. The r^{-5} term does not vanish, but the r^{-6}

* Since the paper went to press it has been proved that $f_7 = -f_8 = -2f_{10}$. A. C. Crehore, Phil. Mag. May 1925, p. 868.

term vanishes for a similar reason to that given for the r^{-4} term, because X, Y, and Z occur in odd degrees in each term of the functions f_7, f_8, f_9, and f_{10}.

This furnishes conclusive proof that the sum of the forces (20) written for each atom in the lattice cannot be set equal to zero, for the coefficient of the r^{-5} term does not vanish, and no adjustment of the size of the cube edge is possible that will make the whole force vanish and produce a stable condition of equilibrium.

The above reasoning rules out any form of lattice for hydrogen that is symmetrical with respect to a centre. This generalization extends the proof so as to exclude the third form of lattice above enumerated, the body-centred cubic lattice, which has not been given in detail. It is thus easier to say what the form of the crystal of solid hydrogen is not than to construct what it is, but even so, results such as these have a practical value that is far from negative. It seems best at this stage to give some consideration to the carbon atom before resuming the discussion of hydrogen.

Carbon.

The model of the carbon atom that we shall use for purposes of computation was first published in the Philosophical Magazine for May 1922, shown in fig. 1, p. 887, and described on p. 890. Some changes * have been made in some of the other atoms shown at that time in this figure but not in that of carbon, which is shown here in fig. 3 in two views—an axial and an equatorial view.

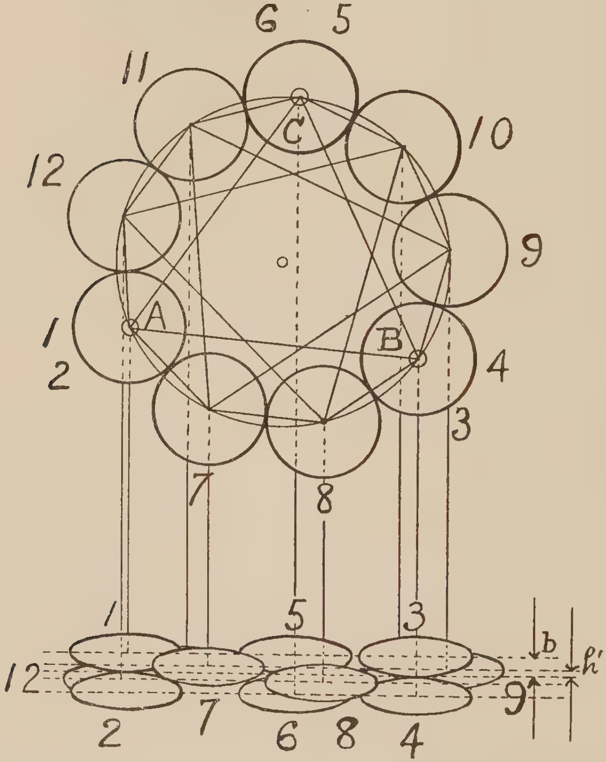
One of the reasons for choosing carbon for investigation here is that there are no isotopes known for carbon, and this is certainly not true for lithium and probably not for glucinum and boron, the next atoms in order of atomic number, excepting helium that forms no compounds. Another reason is the perfect symmetry of the model of the atom, the fact that it has the form of a ring containing three alpha-particles and no hydrogen atoms, and that there exist at least two crystals, the diamond and graphite, with which theoretical results may be compared and checked. And, again, carbon forms many compounds with hydrogen, which may ultimately be worked out in some detail when there has been a satisfactory confirmation of the theory by the use of crystals.

The three positive charges, A, B, and C of fig. 3, in the three alpha-particles of the carbon atom form a perfect equilateral

* See fig. 2, p. 37, 'The Progress of Atomic Theory,' A. C. Crehore.

triangle in the equatorial plane of the atom. There are then twelve negative electrons, six of them, 1–6, belonging to the alpha-particles, and six, 7–12, serving as the so-called connecting electrons to bind the structure together. There are thus four perfect equilateral triangles of negative electrons,

Fig. 3.



Detail drawing of the Carbon atom in plan and elevation, showing the distances b and h'.

the upper ones, 1, 3, and 5, in the alpha-particles forming the first, the lower ones, 2, 4, and 6, the second, the upper three connecting electrons, 7, 9, and 11, the third, and the lower three, 8, 10, and 12, the fourth triangle. The connecting electrons are supposed to be staggered alternately up and down all around the ring; that is to say, they are not exactly in the equatorial plane, but located at about half the distance

from it that the electrons in the alpha-particles have. The reason for this separation from the equator is the mutual repulsion of the adjacent negative connecting electrons. This repulsion is balanced, however, by the strong attraction they have for the alpha-particles, each having an effective charge of $+2e$.

In the free carbon atom the common distance of all electrons in the alpha particles from the equator is the same, equal to b, the semi-minor axis of the negative electron very approximately. Similarly the connecting electrons have the same distance from the equator, the one as the other, say equal to h', which differs from b and is thought to be about half the value of b. When the atom forms part of a molecule, however, instead of being free, the upper distances, b and h', change to b_2 and h_2', and the lower distances are $-b_1$ and $-h_1'$, each of which differs by a very small amount from b and h'. The differences, $D=b_2-b_1$ and $H=h_2'-h_1'$, which are zero in a free atom, become appreciable when a molecule is formed. A finite value for D is in fact demanded in order that a molecule may be formed.

The expression for the force that has been derived from the electrostatic forces for a second such carbon atom acting upon the positive charge only of the first carbon atom at the origin of coordinates, the axis of the latter coinciding with the z-axis, is as follows:—

$$\underset{\substack{C_2 \text{ on} \\ 3 \text{ positive charges} \\ \text{of first atom.}}}{F_z} = \frac{e^2}{k}\{36f_1(D+H)r^{-3} + 108f_2[(b^2+h'^2)-\rho a^2]r^{-4}\ldots\}, \quad (29)$$

where the functions, f_1 and f_2, are identical with those determined in the case of hydrogen given above by (10) and (11). The corresponding expression for hydrogen was given in (9). If in (29) we should make $h'=b$ and $H=D$, then it is seen that the force becomes exactly 36 times that of (9), 36 being the square of the atomic number of carbon. But h' is not equal to b, nor H to D in the carbon atom, and it is here that the character of the expression for carbon differs from that for hydrogen. Otherwise we might form the same conclusions from this equation that were drawn from (9) for hydrogen.

Without making any use of (29) for the moment, let us pass immediately to the second condition which must be satisfied by any form of lattice structure. For this we require the force of a second carbon atom upon the whole

of the first atom at the origin. This has been proven to be as follows:—

Second carbon atom on first carbon atom.

$$\begin{aligned} F_z = \frac{e^2}{k}\{&27f_3(D+H)^2r^{-4} \\ &+27[f_4(b^2+h'^2)-f_5\rho a^2-f_6\rho a^2](D+H)r^{-5} \\ &+135[f_7(b^2+h'^2)^2+(f_8+2f_9)\rho a^2(b^2+h'^2) \\ &-2f_{10}\rho^2a^4]r^{-6}\ldots\}, \quad . \quad .. \quad (30) \end{aligned}$$

where the functions f_3 to f_{10} are given by (21) to (28), being identical with those obtained in the case of hydrogen.

Here also it is seen that, if $h'=b$ and $H=D$, equation (30) is exactly 36 times (20), the corresponding expression for hydrogen. But this is not true, a fact which gives rise to some differences between the two equations. However, because the functions f_3 to f_{10} are the same as before, we find that, when the forces of a single pair of atoms on opposite sides of the selected atom at the same distance and having parallel axes are added together, both the r^{-4} and the r^{-6} terms of (30) vanish, leaving only the r^{-5} term. As pointed out above, this proves conclusively that no form of lattice having a centre of symmetry can satisfy the condition that the sum of the forces for the lattice shall be zero. From this it follows that carbon will neither crystallize in the form of a simple cubic lattice, a face-centred cubic, nor a body-centred cubic lattice. This conclusion is undoubtedly true, the structure of both the diamond and graphite being different from the lattices named.

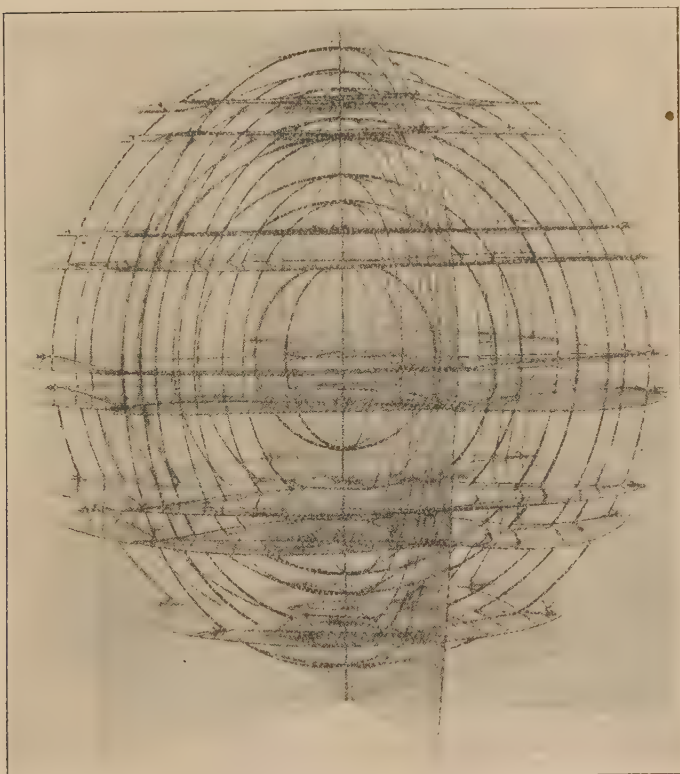
There is a double reason why the simple cubic lattice will not answer, namely that neither the first nor the second condition is satisfied, the first condition involving the sum of equations like (29) for the lattice, and the second like (30). The sum of (29) comes out positive for the cubic lattice, whereas it must be negative as pointed out. The sum of (30) must be zero, and this condition cannot be satisfied. On the other hand, the face-centred cubic lattice satisfies the first condition, since the sum of (29) is negative as shown. The sum of (30), however, cannot be zero.

Now it is well known that there are a number of elements which crystallize as a face-centred lattice. It may be presumed, therefore, that the fundamental equation for such elements corresponding to (30) will contain in the r^{-4} and r^{-6} terms functions of X, Y, and Z including a constant term that does not change sign by a reversal of their signs. Aluminium is an example of an element that forms a face-centred lattice, and aluminium happens to be the atom of highest atomic number for which a model has been

constructed. It can already be seen from its model that such terms as referred to make their appearance in the case of aluminium, and we may expect that this second condition that is not satisfied by carbon will be fulfilled by aluminium, thus allowing the formation of the face-centred lattice. But the case of aluminium is not completed, and no more can be stated here than that it seems probable that it will yield a face-centred lattice.

The Diamond Lattice.

Fig. 4 A.

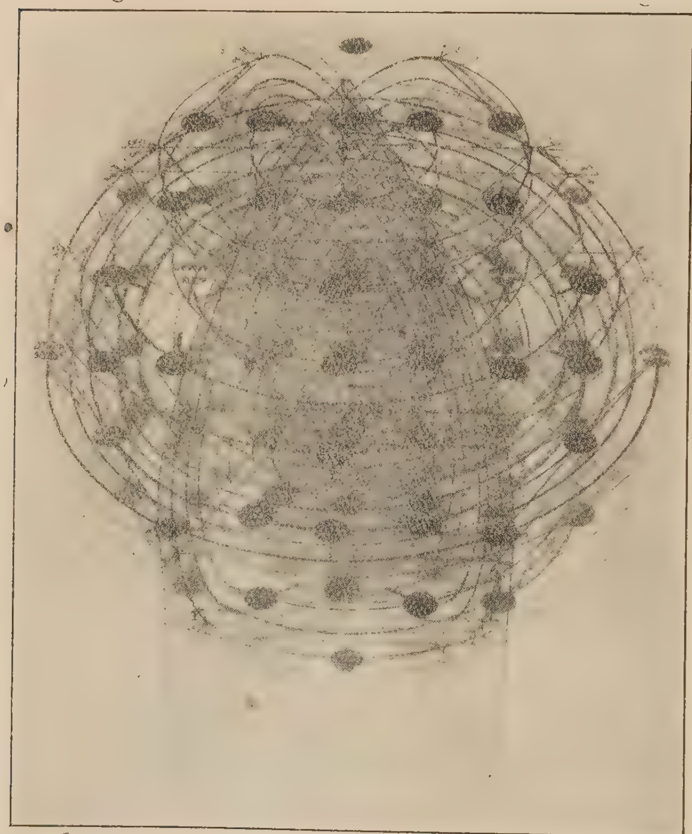


Side view of the model of the Diamond Lattice, showing eight concentric spheres of atoms.

A model of the diamond lattice constructed along the same lines as that of the simple cubic lattice above described and shown in figs. 2 A and 2 B is pictured in figs. 4 A

and 4 B in two different views. This lattice consists of two interpenetrating face-centred cubic lattices displaced along the direction of the diagonal of the cube by a distance from each other of 3/4 the altitude of the regular tetrahedron, whose base is one of the elementary equilateral

Fig. 4 B.



View of the model of the Diamond Lattice from a point which shows the cubical structure.

triangles. There are nine of the (1 1 1) planes shown in the model, which include 98 atoms in 8 concentric spheres surrounding the selected atom. A scheme for this lattice is shown in Table X. The first column gives the number of the (1 1 1) plane, and the second column the distance of

TABLE X.

Diamond Lattice.

No. Plane.	z of plane.	Like Fig. 1 A.	Like Fig. 1 C.	Like Fig. 1 B.
-8	$-\frac{4}{3}\sqrt{3}\,l$			,,
-7	$-\frac{13}{12}\sqrt{3}$,,			,,
-6	$-\sqrt{3}$,,	,,		
-5	$-\frac{3}{4}\sqrt{3}$,,	,,		
-4	$-\frac{2}{3}\sqrt{3}$,,		,,	
-3	$-\frac{5}{12}\sqrt{3}$,,		,,	
-2	$-\frac{1}{3}\sqrt{3}$,,			,,
-1	$-\frac{1}{12}\sqrt{3}$,,			,,
0	0	,,		
$+1$	$+\frac{1}{4}\sqrt{3}$,,	,,		
$+2$	$+\frac{1}{3}\sqrt{3}$,,		,,	
$+3$	$+\frac{7}{12}\sqrt{3}$,,		,,	
$+4$	$+\frac{2}{3}\sqrt{3}$,,			,,
$+5$	$+\frac{11}{12}\sqrt{3}$,,			,,
$+6$	$+\sqrt{3}$,,	,,		
$+7$	$+\frac{5}{4}\sqrt{3}$,,	,,		
$+8$	$+\frac{4}{3}\sqrt{3}$,,		,,	

the plane from the zero plane, namely the value of z, in terms of the elementary cube edge. The last three columns indicate the arrangements of the axes of the atoms as being like either fig. 1 A, the zero plane, fig. 1 B, plane -1, or fig. 1 C, plane $+2$. Because the lattice is, so to speak, two face-centred lattices together at a distance $\frac{1}{4}\sqrt{3}\,l$ apart (the

wider interval in the model) adjacent planes separated by a wide interval are identical, namely plane 0 is like plane +1, +2 like +3, +4 like +5, and so on.

Table XI. gives the radii of 24 concentric spheres in the

TABLE XI.

Diamond Lattice.

Sphere No. Diamond Lattice.	Radius sphere diamond.	Corresponding Sphere No. Cubic Lattice. Double radius.	Sphere No. Diamond Lattice.	Radius sphere diamond.	Corresponding Sphere No. Cubic Lattice. Double radius.
1	$\frac{1}{4}\sqrt{3} = 0{\cdot}4330\ l$		13	$\frac{1}{4}\sqrt{51} = 1{\cdot}7854\ l$	
2	$\frac{1}{2}\sqrt{2} = 0{\cdot}7071$,,	2	14	$\frac{1}{2}\sqrt{14} = 1{\cdot}8709$,,	13
3	$\frac{1}{4}\sqrt{11} = 0{\cdot}8292$,,		15	$\frac{1}{4}\sqrt{59} = 1{\cdot}9203$,,	
4	$1{\cdot}0000$,,	4	16	$2 = 2{\cdot}0000$,,	14
5	$\frac{1}{4}\sqrt{19} = 1{\cdot}0897$,,		17	$\frac{1}{4}\sqrt{67} = 2{\cdot}0464$,,	
6	$\frac{1}{2}\sqrt{6} = 1{\cdot}2248$,,	6	18	$\frac{3}{2}\sqrt{2} = 2{\cdot}1213$,,	16
7	$\frac{3}{4}\sqrt{3} = 1{\cdot}2990$,,		19	$\frac{5}{4}\sqrt{3} = 2{\cdot}1651$,,	
8	$\sqrt{2} = 1{\cdot}4142$,,	7	20	$\sqrt{5} = 2{\cdot}2361$,,	18
9	$\frac{1}{4}\sqrt{35} = 1{\cdot}4790$,,		21	$\frac{1}{4}\sqrt{83} = 2{\cdot}2776$,,	
10	$\frac{1}{2}\sqrt{10} = 1{\cdot}5812$,,	9	22	$\frac{1}{2}\sqrt{22} = 2{\cdot}3452$,,	20
11	$\frac{1}{4}\sqrt{43} = 1{\cdot}6394$,,		23	$\frac{1}{4}\sqrt{91} = 2{\cdot}3849$,,	
12	$\sqrt{3} = 1{\cdot}7321$,,	11	24	$\sqrt{6} = 2{\cdot}4495$,,	21

diamond lattice including 488 atoms. The last column gives the number of the sphere in the simple cubic lattice of Table IV. which is identical in all respects with the sphere of the diamond, provided only the linear dimensions of the simple cubic sphere are each divided by 2, as above

explained. Table XII. gives a more complete specification of the diamond lattice including 24 spheres, plane by plane

TABLE XII.

Diamond Lattice.

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos α.	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3Z\zeta+\cos\alpha)p^{-3}$.
	$\frac{1}{4}\sqrt{3}$ l	−1	1	$-\frac{1}{3}$	3			
	,, ,,	+1	0	1	1	4	4	−65·6896
2	$\frac{1}{2}\sqrt{2}$,,	0	1	$-\frac{1}{3}$	6			
,,	,, ,,	+2	1	,,	3	12	16	−88·3170
3	$\frac{1}{4}\sqrt{11}$,,	3	1	,,	3			
,,	,, ,,	−1	2	1	3			
,,	,, ,,	+1	1	$-\frac{1}{3}$	6	12	28	−75·5589
4	l	+2	2	1	3	6	34	..
5	$\frac{1}{4}\sqrt{19}$,,	−3	2	1	3			
,,	,, ,,	−1	3	$-\frac{1}{3}$	6			
,,	,, ,,	+3	1	,,	3	12	46	−77·5112
6	$\frac{1}{2}\sqrt{6}$,,	0	2	,,	6			
,,	,, ,,	+2	3	,,	6			
,,	,, ,,	+4	1	,,	3	24	70	−68·8018
7	$\frac{3}{4}\sqrt{3}$,,	−5	0	1	1			
,,	,, ,,	−3	3	$-\frac{1}{3}$	6			
,,	,, ,,	+1	2	,,	6			
,,	,, ,,	+3	2	1	3	16	86	−73·7084
8	$\sqrt{2}$,,	0	3	1	6			
,,	,,	+4	2	1	3	12	98	,,
9	$\frac{1}{4}\sqrt{35}$,,	−5	1	$-\frac{1}{3}$	6			
,,	,, ,,	−1	4	,,	6			
,,	,, ,,	+1	3	1	6			
,,	,, ,,	+3	3	$-\frac{1}{3}$	6	24	122	−69·4165

TABLE XII. (*continued*).

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos α.	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3Z\zeta+\cos\alpha)p^{-3}$.
10	$\frac{1}{2}\sqrt{10}\,l$	+2	4	$-\frac{1}{3}$	6			
"	" "	+4	3	"	6	24	146	−73·4643
11	$\frac{1}{4}\sqrt{43}$ "	−3	4	"	6			
"	" "	−1	5	1	3			
"	" "	+5	1	$-\frac{1}{3}$	3	12	158	−71·6907
12	$\sqrt{3}$ "	+2	5	1	3			
"	" "	+6	0	1	1	8	166	"
13	$\frac{1}{4}\sqrt{51}$ "	−5	2	$-\frac{1}{3}$	6			
"	" "	−3	5	1	3			
"	" "	−1	6	$-\frac{1}{3}$	6			
"	" "	+3	4	"	6			
"	" "	+5	2	1	3	24	190	−72·9035
14	$\frac{1}{2}\sqrt{14}$ "	0	4	$-\frac{1}{3}$	12			
"	" "	+2	6	"	6			
"	" "	+4	4	"	6			
"	" "	+6	1	"	6	48	238	−73·6017
15	$\frac{1}{4}\sqrt{59}$ "	−7	1	"	3			
"	" "	−5	3	1	6			
"	" "	−3	6	$-\frac{1}{3}$	6			
"	" "	+1	4	"	12			
"	" "	+3	5	1	3			
"	" "	+5	3	$-\frac{1}{3}$	6	36	274	−74·2527
16	2 "	+4	5	1	3	6	280	"
17	$\frac{1}{4}\sqrt{67}$ "	−7	2	1	3			
"	" "	−1	7	$-\frac{1}{3}$	3			
"	" "	+3	6	"	6	12	292	−75·6740

TABLE XII. (*continued*).

No. Sphere.	Radius Sphere.	No. Plane.	No. Circle.	Cos α.	No. Atoms, Circle.	No. Atoms, Sphere.	Total Atoms.	$\Sigma(-3Z\zeta+\cos\alpha)p^{-3}$.
18	$\frac{3}{2}\sqrt{2}\ l$	0	5	$-\frac{1}{3}$	6			
,,	,, ,,	+2	7	,,	3			
,,	,, ,,	+4	6	,,	6			
,,	,, ,,	+6	2	,,	6	36	328	−73·7186
19	$\frac{5}{4}\sqrt{3}$,,	−7	3	,,	6			
,,	,, ,,	−3	7	,,	3			
,,	,, ,,	−1	8	1	6			
,,	,, ,,	+1	5	$-\frac{1}{3}$	6			
,,	,, ,,	+5	4	,,	6			
,,	,, ,,	+7	0	1	1	28	356	−72·6886
20	$\sqrt{5}$,,	+2	8	1	6			
,,	,, ,,	+6	3	1	6	24	380	,,
21	$\frac{1}{4}\sqrt{83}$,,	−5	4	$-\frac{1}{3}$	12			
,,	,, ,,	−3	8	1	6			
,,	,, ,,	−1	9	$-\frac{1}{3}$	6			
,,	,, ,,	+3	7	,,	3			
,,	,, ,,	+5	5	1	3			
,,	,, ,,	+7	1	$-\frac{1}{3}$	6	36	416	−72·1216
22	$\frac{1}{2}\sqrt{22}$,,	+2	9	,,	6			
,,	,, ,,	+4	7	,,	3			
,,	,, ,,	+8	1	,,	3	24	440	−72·6855
23	$\frac{1}{4}\sqrt{91}$,,	−7	4	,,	6			
,,	,, ,,	−3	9	,,	6			
,,	,, ,,	+3	8	1	6			
,,	,, ,,	+5	6	$-\frac{1}{3}$	6	24	464	−72·1410
24	$\sqrt{6}$,,	0	6	1	6			
,,	,, ,,	+4	8	1	6			
,,	,, ,,	+8	2	1	3	24	488	,,

and circle by circle in these planes. The last column gives the important total summation of f_1 of equation (10) when multiplied by p^{-3}, where $p=r/l$, for all the spheres from the first to the given sphere inclusive. By this last column it is seen that the first sphere gives the largest sum, but that for a very accurate value for an infinite lattice probably more than 24 spheres should be computed.

Table XIII. gives the sum of $p^{-4}f_2$, where f_2 is given by (11) above. This Table includes but 6 spheres and 70 atoms. The more rapid decrease in this sum per sphere with increasing sphere number is due to the higher order of the term, r^{-4} instead of r^{-3} above, so that an approximate value for an infinite lattice is obtained from 6 spheres.

Table XIII.

Diamond Lattice.

No. sphere.	No. atoms.	$\Sigma p^{-4}f_2$ sphere.	$\Sigma p^{-4}f_2$ total.
1	4	$-44{\cdot}949$	$-44{\cdot}949$
2	12	0	$-44{\cdot}949$
3	12	$-10{\cdot}952$	$-55{\cdot}901$
4	6	0	$-55{\cdot}901$
5	12	$+0{\cdot}3515$	$55{\cdot}55$
6	24	0	$-55{\cdot}55$
Total......	70		

By the use of the sums in Tables XII. and XIII. it is possible to write down the sum of equation (29) for the whole diamond lattice. The total force upon the positive charge of the selected carbon atom at the origin due to the whole surrounding lattice of carbon atoms is, therefore, approximately

$$\underset{\substack{\text{Diamond lattice}\\ \text{on 3 + charges.}}}{\mathrm{F}_z} = \frac{e^2}{k}\{36(-72{\cdot}14)(\mathrm{D}+\mathrm{H})l^{-3} + 108(-55{\cdot}55)\left[(b^2+h'^2)-\rho a^2\right]l^{-4}\ldots\}. \quad (31)$$

The force upon just one positive charge of one of the

alpha-particles of one carbon atom is, therefore, one third of the above force, and this may be equated to the expression in (12) above because the same reasoning applies here as there, the value of ρ_z having been derived from the properties of the electron itself. Hence we find the equation representing the first condition that must be satisfied by the carbon lattice, namely

$$-865{\cdot}68(\mathrm{D}+\mathrm{H})l^{-3}-1999{\cdot}8[(b^2+h'^2)-\rho a^2]l^{-4} = -30{\cdot}7\times10^{24}\mathrm{D}. \quad (32)$$

The second condition is that the sum of the forces of all atoms in the lattice upon the whole of each and every atom in the lattice shall be equal to zero. If the lattice were constructed of hydrogen atoms the sum of the forces given by (20) above must be zero, but if constructed of carbon atoms the sum of the forces given by (30) must vanish. Since both these equations involve the same functions of X, Y, and Z, it seems best to consider them together in order that their differences may be emphasized. The sums of the functions f_3 to f_{10} given in (21) to (28) are found for the diamond lattice to be as follows:—Since f_3 is the coefficient of an r^{-4} term, it has been summed for six concentric spheres including 70 atoms, but f_4, f_5, and f_6 have been summed for only three spheres, 28 atoms, these being coefficients of an r^{-5} term; while f_7 to f_{10} have been summed for but two spheres, 16 atoms. We find for the diamond form of lattice

$$\Sigma f_3 r^{-4} = 89{\cdot}218\, l^{-4}, \quad (33)$$
$$\Sigma f_4 r^{-5} = -1022{\cdot}597\, l^{-5}, \quad (34)$$
$$\Sigma (f_5+f_6) r^{-5} = -1015{\cdot}575\, l^{-5}, \quad (35)$$
$$\Sigma f_7 r^{-6} = -2217{\cdot}496\, l^{-6}, \quad (36)$$
$$\Sigma (f_8+2f_9) r^{-6} = 1917{\cdot}83\, l^{-6}, \quad (37)$$
$$\Sigma f_{10} r^{-6} = 775{\cdot}374\, l^{-6}. \quad (38)$$

Substituting these summations in (20) gives the force of the whole lattice of hydrogen atoms upon the one hydrogen atom as

$$\underset{\substack{\text{Diamond form}\\ \text{of lattice}\\ \text{on H.}}}{\mathrm{F}_z} = \frac{3e^2}{k}\{89{\cdot}218\mathrm{D}^2l^{-4}-1022{\cdot}597b^2\mathrm{D}l^{-5} +507{\cdot}788\rho a^2\mathrm{D}l^{-5}-11087{\cdot}48b^4l^{-6} +4794{\cdot}58\rho a^2b^2l^{-6}-1938{\cdot}44\rho^2a^4l^{-6}\} = 0. \quad (39)$$

And substituting them in (20) gives the force of the whole lattice of carbon atoms upon one carbon atom as

Diamond lattice on C.

$$F_z = \frac{27e^2}{k}\{89\cdot218(D+H)^2l^{-4}-1022\cdot597(b^2+h'^2)(D+H)l^{-5} \\ +1015\cdot58\rho a^2(D+H)l^{-5}-11087\cdot48(b^2+h'^2)^2l^{-6} \\ +9589\cdot15\rho a^2(b^2+h'^2)l^{-6}-7753\cdot74\rho^2a^4l^{-6}\}=0. \quad . \quad . \quad . \quad (40)$$

Equation (39) proves that the hydrogen atom does not fulfil the necessary conditions to enable it to form a crystal in the form of the diamond lattice, and so this is quickly disposed of. For, after putting in the numerical * values

$$b^2=10^{-26} \quad \text{and} \quad \rho a^2=4\cdot484\times10^{-26}, \quad . \quad . \quad . \quad (41)$$

multiplying each term by l^6 and dividing by the coefficient of D^2l^2, we have from (39) the quadratic equation in terms of Dl as follows:

$$D^2l^2+14\cdot05\times10^{-26}Dl+95\cdot0\times10^{-52}=0; \quad . \quad . \quad (42)$$

whence

$$Dl=(-7\cdot025\pm\sqrt{-45\cdot65})10^{-26}, \quad . \quad . \quad (43)$$

an imaginary quantity. Both D and l must have real values to satisfy the requirements for the lattice, and hence it was rightly concluded above that hydrogen cannot form crystals in a form like that of diamond.

Let us, therefore, turn to the carbon atom lattice in the form of the diamond. The two conditions to be satisfied are (32) and (40). As pointed out before, the force in (40) would be exactly 36 times that in (39) for hydrogen, if we put $h'=b'$ and $H=D$. If this were true we should be obliged to conclude as above for hydrogen that the diamond form of lattice will not satisfy the equation for carbon either. From this it becomes evident that the important thing is the location of the connecting electrons, that is to say, their distance from the equatorial plane of the carbon atom, the quantity h' in the equations.

Now the value of h' for a connecting electron is substantially a fixed value, estimated to be about one half of b, the semi-minor axis of the electron at all times, but it varies to a very minute extent in the different forms of molecule just as b varies. The value found for h' should be very closely the same whatever form of molecule is examined, whether diamond, graphite, CH_4, C_2H_4, and so on; but the

* Phil. Mag. May 1925, p. 888, eq. (9).

values found for D and H, the small differences between the upper and lower distances should vary considerably from one form to another, since they are connected with the energies of formation and dissociation of the molecule in question. It may be seen from a study of the manner in which the forces act upon the electrons shown by the drawing of the model of the carbon atom in fig. 3 that H will be approximately the same proportion of D that h' is of b. Let us assume for a first approximation, which will be slightly modified as we proceed, that this ratio is exactly one half. If so, equations (32) and (40) contain only D and l as the unknown quantities, since b^2 and ρa^2 are known numerically, as given in (41) above. Consequently they may be solved very readily for both the unknown quantities, D and l, since under this hypothesis (40) reduces to a quadratic in terms of Dl similar to (42). The value obtained for the cube edge, l, however, under the supposition that $h' = 0{\cdot}5\,b$, does not come out exactly equal to the experimental value of l for the diamond. This ratio assumed as 0·5 above requires to be slightly altered to approximately

$$h' = 0{\cdot}42\,b \quad \text{and} \quad \mathrm{H} = 0{\cdot}42\,\mathrm{D}, \quad . \quad . \quad . \quad (44)$$

when the solution of the two simultaneous equations (32) and (40) gives exactly

$$l = 3{\cdot}56 \times 10^{-8}\ \text{cm.} \quad \text{and} \quad \mathrm{D} = -11{\cdot}9 \times 10^{-18}\ \text{cm.}, \quad (45)$$

the former being the experimental value for the cube edge. In fact, when $l = 3{\cdot}56 \times 10^{-8}$ cm. and h' and H as in (44) are substituted in (32), we find immediately

$$\mathrm{D} = -11{\cdot}92 \times 10^{-18}\ \text{cm.} \quad . \quad . \quad . \quad . \quad (46)$$

When they are substituted in (40) we have the quadratic equation

$$\mathrm{D}^2 + 7{\cdot}4296 \times 10^{-18}\mathrm{D} = 52{\cdot}88 \times 10^{-36}, \quad . \quad . \quad (47)$$

from which

$$\mathrm{D} = -11{\cdot}88 \times 10^{-18}\ \text{cm.} \quad \text{or} \quad +4{\cdot}45 \times 10^{-18}\ \text{cm.} \quad (48)$$

The negative values of D in (46) and (48) are very closely the same, and a value of h' very slightly in excess of $0{\cdot}42\,b$ will make the two values of D identical. This value for D incidentally is not far different from that found for the hydrogen molecule in the previous paper *, namely $14{\cdot}47 \times 10^{-18}$ cm.

Both conditions are, therefore, perfectly satisfied by the

* Phil. Mag. May 1925, p. 882, eq. (66).

form of the diamond lattice, by its absolute dimensions, and by the model of the carbon atom shown in fig. 3, and we may conclude on theoretical grounds alone that the carbon atom may form such a crystal.

The negative value of D shows that the force upon the positive charge is positive according to (12), that is in an upward direction away from the base and toward the apex of the regular tetrahedron of atoms forming the first surrounding sphere in the lattice. Hence the electron on the side of this apex is the one that is compressed, while that on the side toward the base is the one that is expanded.

This completes the account of the diamond, and we would naturally turn next to graphite for still further confirmation of these ideas. Graphite, however, does not come under the head of the cubic or isometric system of crystals, and as yet its study has not been completed. There is the problem of determining the directions of the axes of each atom in the crystal before any of the above equations for the carbon atom may be applied. We shall conclude the paper by making some suggestions as to a possible form for a crystal of solid hydrogen.

The Hydrogen Lattice.

It has been shown above that hydrogen will not crystallize in the form of any one of the four lattices of the cubic system considered. The question remains, "how does it crystallize?" The investigation has not proceeded far enough to enable this question to be answered with definiteness, but there are certain indications worth noting. The first of these is the measured density of liquid hydrogen. Dewar gives it as 0·070 at $-252°$ C., but the writer has found no record of the density of solid hydrogen. Lacking this, it may be assumed that the density is roughly 0·08, because the ratio of 8/7 is not far from that which the solid to the liquid form has in a number of the elements.

If hydrogen formed a simple cubic lattice, which it does not, this density would give the cube edge as

$$l = 2{\cdot}75 \times 10^{-8} \text{ cm.}, \quad . \quad . \quad . \quad . \quad . \quad (49)$$

but if it formed a face-centred lattice the same density would give

$$l = 4{\cdot}36 \times 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

and the distance between nearest atoms would be

$$\tfrac{1}{2}\sqrt{2}l = 3{\cdot}08 \times 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad (51)$$

The value found for l to satisfy the first theoretical condition for a face-centred lattice in (19) above is

$$l = 1\cdot05 \times 10^{-8} \text{ cm.}, \quad . \quad . \quad . \quad . \qquad (52)$$

which is so much smaller than either of the above values obtained from the density that both these lattices utterly fail to be satisfactory. This great discrepancy, however, is suggestive because the theory demands a very small distance between nearest atoms and the density demands a large average distance. The suggestion is that a group composed of a small number of atoms, probably four atoms, acts just like a single atom in a manner very analogous to, say, ammonium chloride, where NH_4 behaves as if it were an element ammonium. This in combination with chlorine forms a cubic lattice, although the combination NH_4 has no independent existence as such except as found in combination in some compound. In an analogous manner a group of four hydrogen atoms, H_4, has no independent existence as such because a hydrogen molecule, H_4, is unknown. It no doubt requires the presence of the surrounding atoms in a lattice to complete its stability.

If it is now assumed that such a group of four hydrogen atoms is arranged in the form of a regular tetrahedron, each with its axis pointing toward its centre, then the force upon the positive charge of one atom due to the other three may be found by the use of equation (2) or (4) above, in which

$$Z = \tfrac{1}{3}\sqrt{6}, \quad X = -\tfrac{1}{3}\sqrt{3}, \quad \cos\alpha = -\tfrac{1}{3},$$

$$\zeta = \tfrac{1}{9}\sqrt{6} \text{ (see (3))}, \quad -3Z\zeta + \cos\alpha = -1,$$

whence

$$\underset{3 \text{ atoms.}}{F_z} = \frac{e^2}{k}(-6)\,Dr^{-3}. \quad . \quad . \quad . \quad . \quad . \qquad (53)$$

Equating this to (12), we have

$$\frac{e^2}{k}(-6)\,Dr^{-3} = -\frac{e^2}{k}(30\cdot7 \times 10^{24})\,D, \quad . \quad . \quad . \qquad (54)$$

whence

$$r^{-3} = 5\cdot117 \times 10^{24} \text{ and } r = 0\cdot58 \times 10^{-8} \text{ cm.} \qquad (55)$$

There is evidently no equatorial force upon the positive charge of any one atom of the group because the other three atoms in the tetrahedron give rise to three equal forces in one plane making 120° with each other, thus giving a resultant of zero. Hence the equation (2) or (4), in the

derivation of which this equatorial displacement was assumed to be zero, applies to such a group of atoms as now supposed. The edge of the tetrahedron is, consequently, the very small value, $0{\cdot}58 \times 10^{-8}$ cm., which corresponds very closely with the distance between the two atoms of a single hydrogen molecule, H_2.

An application of equation (20) to the case will give a numerical value of D. We will not carry through a computation of D here, however, but merely note that both the first and second conditions are satisfied by such a tetrahedron of atoms.

The question immediately arises why will such an arrangement not form an independent molecule of H_4. The answer is that there is one condition that is not satisfied, and that is the turning moments of the forces, which must give a definite direction to each atom's axis. The sum of the turning moments of any three atoms of such a tetrahedron upon the fourth atom is zero, because each atom tries to turn its neighbour so that its axis comes into parallelism with itself. The effect of the three upon the one may be represented by three equal vectors in one plane making 120° with each other, whose sum is zero. There is, therefore, no directing influence upon any one atom to hold its axis in any particular direction, and as soon as one begins to turn the translational forces just computed are altered at once, and there is no stability. This rules out the tetrahedron as a stable molecule of H_4 having an independent existence, but it does not prevent it from forming part of a large lattice of atoms, because this lattice may supply just the necessary requirement to satisfy the turning moments and thus give stability to the structure.

Now the distances between the atoms in such a tetrahedron are so small as compared with the distances between such groups in a cubic lattice, that the cube edge may be computed from the density of solid hydrogen as if there were one atom of four times the mass of the hydrogen atom at each corner of the cube. The mass of one elementary cube is then

$$m = 4 \times 1{\cdot}66 \times 10^{-24} = 0{\cdot}08\, l^3, \quad . \quad . \quad . \quad (56)$$

whence

$$l^3 = 83{\cdot}0 \times 10^{-24} \quad \text{and} \quad l = 4{\cdot}36 \times 10^{-8} \text{ cm.} \quad . \quad (57)$$

A possible form for the crystal of solid hydrogen may then be a cubic lattice of about $4{\cdot}36 \times 10^{-8}$ cm. on an edge, at the corners of which are groups of four hydrogen atoms

in the form of a regular tetrahedron of $0{\cdot}58 \times 10^{-8}$ cm. on an edge. This tetrahedron may be thought of as enclosed within a small cube whose edge is $0{\cdot}58 \times 10^{-8}/\sqrt{2} = 0{\cdot}41 \times 10^{-8}$ cm., which is a little more than ten times smaller than the larger elementary cube given by (57).

To work out the forces upon one such group of atoms due to the whole lattice in detail by the use of the equations above given has not been attempted, but nevertheless the points that have been mentioned seem to warrant the suggestions made as to the form of the solid hydrogen lattice.

Conclusion.

In this paper it is considered that an important real contact has been established between this atomic theory and some of the most reliable experimental measurements in the atomic realm, namely the facts that have been revealed in recent years by the use of X-rays in the analysis of crystals. The theory rings true at every point of contact. To arrive at this stage many steps have been required where the going must have seemed blind and the subject to be of an academic character, because the work could not be compared with any experimental data along the way. Now, however, the results seem certain to be of considerable practical value for chemistry.

LXXIII. *A Natural Limit for the Sensibility of Galvanometers. By* GUSTAF ISING *.

IN the number of the Philosophical Magazine for Sept. 1925 W. J. H. Moll and H. C. Burger describe an interesting method of multiplying the sensibility of a galvanometer with the aid of their "Thermo-relay." When very high (25- to 100-fold) magnification of the sensibility of the primary Moll-galvanometer was employed, the registered curve showed small perpetual fluctuations of the zero-position, which by the authors are interpreted as due to microseismic perturbations. But, as shown in the following, there is reason to believe that the main part of these fluctuations were nothing else than the *Brownian fluctuations* of a suspended system, theoretically announced by M. v. Smoluchowsky †.

* Communicated by the Author.

† *Phys. Zeitschr.* xiii. p. 1069 (1912).

I have earlier * discussed the natural limit for the sensibility of some different kinds of instruments (electrometer, galvanometer, balance), which is determined, according to the theory, by these fluctuations, and shall in Parts I. and II. below repeat these considerations in so far as they concern galvanometers. With the aid of the obtained formulas then, in Part III., the curve (d) published by Moll and Burger on page 630 of the volume quoted will be examined.

I.

Consider a movable system, the position of which is determined by a coordinate x and which is tied to the position $x=x_0$ by a directional force A; let $\delta x = x - x_0$ denote the deviation from the zero-position at a certain instant †. If the root-mean-square value of δx is denoted by $\overline{\delta x}$, according to Smoluchowsky (with other notations) the following relation holds:

$$\tfrac{1}{2}A\overline{\delta x^2}=\epsilon,$$

or

$$\overline{\delta x}=\sqrt{\frac{2\epsilon}{A}}, \quad \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ϵ is the mean kinetic energy per degree of freedom of a molecule. At room temperature (18° C.) ϵ has the value $2{\cdot}00\times10^{-14}$ erg. If, for instance, a torsional system is controlled by a directional force $A=10^{-6}\frac{\text{dyne}\times\text{cm.}}{\text{radian}^2}$, eq. (1) gives $\overline{\delta x}=2\times10^{-4}$ radian.

The sensibility (s) of an instrument is now given by the quotient $\frac{\delta x}{\delta i}$, where δi is that change in a physical quantity i (current intensity, potential, etc.) which is to be measured by the instrument, and δx the deviation provoked by this change:

$$s=\frac{\delta x}{\delta i}.$$

As a rule the deviation is not directly given in "absolute"

* G. Ising, *Undersökningar rörande elektrometrar*, i. p. 46 (1917); ii. p. 363 (1919). *Kosmos* p. 69 (1923). In Swedish.

† As a rule x denotes an *angle*. But, of course, the reasoning applies without change to any system with one degree of freedom, the position of which is determined by the parameter x: A is then a *directional force* in *generalized* meaning: $\frac{1}{2}A\delta x^2$ giving the work (in ergs) necessary for a small deviation δx.

units δx (cms., radians, etc.) but in *scale-divisions* $\delta x'$; one has

$$\delta x' = n\delta x,$$

where the factor of proportionality n may be termed the *magnification*. The sensibility, expressed as number of scale-divisions per unit change of i, is then

$$s' = \frac{\delta x'}{\delta i} = ns.$$

When the magnification has been made so great that the Brownian fluctuations of the zero point cover a visual angle which is easily discernible on the scale, there is, as a rule, no gain in pushing it further. The least deviation—we denote it by $(\delta x)_{\min}$— which one may be able to recognize, with confidence, as being really *provoked* (by a changement δi) and not a mere Brownian fluctuation, may be estimated to about $4\overline{\delta x}$:

$$(\delta x)_{\min} = 4\overline{\delta x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This estimation is seen to be justified, if one supposes the magnification so high that $\overline{\delta x'} = \frac{1}{4}$ scale-division ; the fluctuations on each side of the zero-position will then in the mean play over $\frac{1}{2}$ division, and it seems reasonable to demand a deviation of one full scale-division, if it is to be recognized as provoked. Such a magnification should be amply sufficient ; if one supposes good optical definition, so that tenths of a scale-division may be estimated, the limit for useful magnification will probably be reached, at least for trained observers, already when the mean Brownian fluctuation is only one-tenth of a scale-division to either side of the zero position. The smallest single deviation, which with fair probability may be distinguished from a Brownian fluctuation, is then about 0·4 scale-division *.

II.

We now proceed to deduce two known general formulas for the current- and potential-sensibility of galvanometers—pointing out that a similar calculus may be made for other kinds of instruments—and then we apply to them the preceding considerations of the Brownian fluctuations.

* If one is able to follow for some time the fluctuations about a new position of equilibrium (=the provoked deviation), even a deviation *less* than four times the mean Brownian displacement may be established without doubt. In such a case it may be of advantage to carry the magnification somewhat further.

The sensibility $s=\frac{\delta x}{\delta i}$ of an instrument may be written as a quotient

$$\frac{\delta x}{\delta i}=\frac{B}{A}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the denominator A is the directional force and the numerator B a quantity such that $B\delta i$ represents the deflecting moment, provoked by the change δi. For each kind of instrument (electrometer, galvanometer, balance, etc.) one is able to find certain general relations between the factors A and B, which allow interesting conclusions to be drawn concerning the sensibility of such instruments altogether irrespective of their special construction.

We consider here only the behaviour of galvanometers, and thus the letter i in the following always means current strength measured in electromagnetic units. Then we have generally

$$B=\frac{dN}{dx}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where N denotes the flux of magnetic induction through the galvanometer-coils; when x changes, the magnets and the coils move relatively to each other, and the flux varies. A general relation between the B and A of any galvanometer is now obtained by supposing that the damping is *critical*, *i. e.*, just sufficient to make the motion aperiodic, and further, that this damping is wholly brought about by the electromagnetic induction in the coils. In fact, a galvanometer will be almost useless for practical measurements if its damping is far from the critical one; the damping constant λ may not differ from the critical value $\lambda=\omega_0$ (see below) by more than a factor of the magnitude 2 or 3. The neglect of the air-damping in comparison with the electromagnetic one is of minor real importance, and simplifies the formulas.

We introduce the notation: K moment of inertia of the moving system, $p\frac{dx}{dt}$ moment of the frictional forces, T period of oscillation, T_0 the period which would have been obtained without damping (*i. e.*, for $p=0$). The differential equation for the motion of the system may be written

$$\frac{d^2x}{dt^2}+2\lambda\frac{dx}{dt}+(\lambda^2+\omega^2)x=0$$

where
$$\lambda = \frac{p}{2K} = \text{the damping constant,}$$
$$\omega = \frac{2\pi}{T} = \text{,, frequency,}$$
$$\omega_0 = \frac{2\pi}{T_0} = \sqrt{\frac{A}{K}} = \text{,, ,, undamped } (\lambda = 0).$$

One has
$$\lambda^2 + \omega^2 = \omega_0^2.$$

Further, if R is the resistance in the galvanometer circuit,
$$\lambda = \lambda_0 + \lambda_{el} = \lambda_0 + \frac{B^2}{2KR}, \quad . \quad . \quad . \quad . \quad (5)$$

where λ_{el} is the electromagnetic damping from the induction in the coils and λ_0 other possible damping (for instance by the air friction). At the limit of aperiodicity $\lambda = \omega_0$, or
$$\lambda_0 + \frac{B^2}{2KR} = \omega_0,$$

which equation determines the value of B, when K, R, ω_0, and λ_0 are given. The greatest value of B, and therefore also the greatest sensibility, is obtained for $\lambda_0 = 0$. We make this assumption, as already mentioned, to simplify the formulas and thus get the system of equations
$$\left.\begin{aligned} \frac{\delta x}{\delta i} &= \frac{B}{A} = \text{the } \textit{current}\text{-sensibility} \\ \omega_0 &= \sqrt{\frac{A}{K}} = \frac{B^2}{2KR}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

Eliminating B and K, we get the current-sensibility s_i :
$$s_i = \frac{\delta x}{\delta i} = \sqrt{\frac{2R}{A\omega_0}}, \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

and, dividing by R, the potential-sensibility s_v :
$$s_v = \frac{\delta x}{\delta v} = \sqrt{\frac{2}{AR\omega_0}}. \quad . \quad . \quad . \quad . \quad (7b)$$

These are the general formulas for the sensibility of galvanometers (at critical damping), mentioned at the beginning of Part II. By the way of their deduction it is evident that they apply as well to needle-galvanometers as to coil-galvanometers *.

* This must be remembered, if one would make a just comparison between these two kinds of galvanometers.

We now combine them with equations (1) and (2). Inserting in (7) for δx the value

$$(\delta x)_{\min}=4\overline{\delta x}=4\sqrt{\frac{2\epsilon}{A}},$$

we get the corresponding δi and δv

$$\left.\begin{aligned}(\delta i)_{\min}&=4\sqrt{\frac{\epsilon\omega_0}{R}}\\ (\delta v)_{\min}&=4\sqrt{\epsilon\omega_0 R}\end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (8)$$

as the smallest changes in current strength and potential difference, respectively, which should be recognizable by *one* single observation.

If we introduce $\omega_0=\dfrac{2\pi}{T_0}$, $\epsilon=2{\cdot}00\times10^{-14}$ and, instead of electromagnetic units, the practical units ampere, volt, and ohm, denoting by a dash quantities measured in them, we get

$$\left.\begin{aligned}(\delta i')_{\min}&=4{\cdot}48\times10^{-10}\frac{1}{\sqrt{T_0 R'}}\text{ amperes,}\\ (\delta v')_{\min}&=4{\cdot}48\times10^{-10}\sqrt{\frac{R'}{T_0}}\text{ volts}\end{aligned}\right\}. \quad . \quad (9)$$

The current- or potential-changes that correspond to a deviation equal to the mean Brownian fluctuation are one-fourth of the values above, *e. g.* the change in potential difference

$$\overline{\delta v'}=1{\cdot}12\times10^{-10}\sqrt{\frac{R'}{T_0}}\text{ volts.} \quad . \quad . \quad . \quad (10)$$

Supposing, for instance, $R'=50$ ohms, $T_0=2$ sec., we get

$$(\delta i')_{\min}=4{\cdot}48\times10^{-11}\text{ amp.}$$
$$(\delta v')_{\min}=2{\cdot}24\times10^{-9}\text{ volt.}$$
$$\overline{\delta v'}=5{\cdot}60\times10^{-10}\quad\text{,,}$$

It is seen that the natural limit for a galvanometer's sensibility is almost surprisingly low. In the literature one finds several reports of (needle-) galvanometers with considerably higher sensibility. One may safely conjecture that in them the useful magnification was vastly surpassed or, in other words, that their reported high sensibility was made illusory by variations of the zero, perhaps already by variations caused by external disturbances but in any case by the Brownian fluctuations.

III.

We now turn to the question whether these fluctuations have manifested themselves in the experiments of Moll and Burger. In order to examine this I photographed their curve (d), obtained with 100 times relay-multiplication *, and magnified it still 10·3 times by projection. The middle-line of the then obtained rather thick curve-image was traced by a pencil, and the fluctuating distance (y) of this line from a straight mean zero-line (x-axis) was measured for some hundred points on the curve. Three sections of the curve were treated separately, namely (1) the whole length on the left side of the great provoked deviation † ; (2) the whole length between this and the small deviation ; (3) about two-thirds of the length to the right of the small deviation ‡. The x-axis was drawn by eye to coincide as near as possible with the mean of the fluctuating curve ; on section (1) it came out feebly inclined to the horizontal boundary-line of the figure, for sections (2) and (3) a common x-axis was drawn, which was very nearly horizontal.

For every millimetre on the x-axis the corresponding y was measured by a millimetre-scale (tenths estimated), and these y-values—reckoned positive upwards (y_+) and negative downwards (y_-)—tabulated. The treatment of these figures will be clear from the following data concerning the longest section (2): number of measured points 390; $\Sigma y_+ = 358{\cdot}0$ mm.; $\Sigma y_- = -253{\cdot}0$; thus $\Sigma y = 105{\cdot}0$ and the arithmetical mean

$\bar{y} = \frac{\Sigma y}{390} = 0{\cdot}27$ mm., which figure shows that the x-axis had happened to be drawn 0·27 mm. too low. This was corrected by adding $-0{\cdot}3$ to every tabulated y-value ; the figures thus obtained represent the fluctuations Δ, the sum of their squares is $\Sigma\Delta^2 = 1524{\cdot}6$ and the mean square value

$\overline{\Delta^2} = \frac{1524{\cdot}6}{390} = 3{\cdot}91$ mm². In the same way it was found : for the section (1) with 190 measured points $\bar{y} = -0{\cdot}18$ mm., and thus the y-correction $= +0{\cdot}2$, $\Sigma\Delta^2 = 778{\cdot}1$, and $\overline{\Delta^2} = 4{\cdot}10$ mm².; for the short section (3) with only 105 points $\bar{y} = 0{\cdot}18$, $\Sigma\Delta^2 = 343{\cdot}5$ and $\overline{\Delta^2} = 3{\cdot}27$ mm².

* Fig. I (d), Phil. Mag. l. p. 630 (1925).

† Compare fig. 1 (d) *loc. cit.*

‡ The last bit of the curve was left out because its mean course there shows an upward deflexion, easily visible in the enlargement, and probably due to some external disturbance.

For all three sections together we have $\Sigma\Delta^2 = 2646{\cdot}2$ mm^2., $\overline{\Delta^2} = \frac{\Sigma\Delta^2}{685} = 3{\cdot}86$ mm^2., and thus the mean fluctuation

$$\overline{\Delta} = \sqrt{\overline{\Delta^2}} = 1{\cdot}97 \text{ mm.}$$

The great deviation on Moll's and Burger's curve, provoked by a potential difference of 10×10^{-8} volt, possessed on the enlarged curve a (mean) ordinate $y = 213{\cdot}5$ mm.; the deviation of 1·97 mm. thus corresponds to

$$\frac{1{\cdot}97}{213{\cdot}5} \cdot 10^{-7} = 9{\cdot}22 \times 10^{-10} \text{ volt,}$$

or $$\overline{\delta v'}_{\text{observed}} = 9{\cdot}22 \times 10^{-10} \text{ volt.}$$

We will now compare this value with that calculated by formula (10). This calculation will, of course, be somewhat uncertain, as only approximate statements as to the value of R' and T_0 are given: "this galvanometer has a time of indication of less than two seconds, its resistance is about 50 ohms" (on p. 629 of the quoted paper). It is probable, both from Dr. Moll's earlier description of the galvanometer*, and from the published curves, that the galvanometer was used with critical damping; in this case a provoked deviation will reach its end-value to within $\frac{1}{2}$ per cent. in a time $= 1{\cdot}18\ T_0$. Supposing this to be the meaning of the "time of indication" and putting it $= 1{\cdot}9$ sec.†, we get $T_0 = 1{\cdot}6$ sec. Assuming further, that the external resistance in the circuit was small, we may put $R' = 50$, and thus obtain

$$\overline{\delta v'}_{\text{calc.}} = 1{\cdot}12 \times 10^{-10} \sqrt{\frac{50}{1{\cdot}6}} = 6{\cdot}3 \times 10^{-10} \text{ volt.}$$

This being about two-thirds of $\delta v'_{\text{obs.}}$, it seems fairly sure that the observed fluctuations in the main were Brownian fluctuations of the primary galvanometer, and only to some small extent due to external perturbations, perhaps microseismic ones such as supposed by Moll and Burger ‡. This fact demonstrates very clearly what an admirable stability and freedom from disturbances the constructors have been able to give both to the galvanometer and to the thermo-relay, their combination approaching the theoretical limit of a galvanometer's sensibility.

Physical Laboratory of the University.
Stockholm, October, 1925.

* Proc. Phys. Soc. xxxv. p. 253 (1923).

† The time of indication should be *less* than two sec.

‡ On the published curve (*d*), enlarged, there is scarcely to be found any support for the assumption of a regular *period* of the fluctuations.

LXXIV. *The Efficiency of β-ray Recoil of Radium C from Radium B.* By A. W. Barton, *M.A., B.Sc., Trinity College, Cambridge**.

Introductory.

EXPERIMENTS on the β-ray recoil of Radium C from Radium B have previously been performed by Russ and Makower † and Muszkat ‡. The former obtained efficiencies of about 0·1 per cent. from a surface of Radium B obtained by exposing a platinum disk to Radium Emanation in the usual way, and the latter using a surface of Radium B prepared by distillation in a vacuum claimed to have obtained values up to 50 per cent.

Recently Jacobsen § has carried out a determination of the half-period of Radium C′ by a method which depends for its success on obtaining an efficient β-ray recoil. In repeating this method with certain modifications, it was thought desirable first of all to investigate thoroughly the phenomenon of β-ray recoil, and the present experiments were performed with that aim in view. Although the conditions were similar the value of the efficiency obtained is considerably lower than that claimed by Muszkat, but as will be shown later it seems to be theoretically reasonable, and moreover an explanation is put forward to account for the discrepancy between the results of these experiments and those obtained by Muszkat.

A Discussion of the Conditions necessary for an Efficient β-ray Recoil.

When an atom of Radium B disintegrates emitting an electron the residual atom Radium C receives a velocity in the opposite direction. Taking $1{\cdot}7\times10^{10}$ cm. per sec. as a mean value of the velocity of the electron, that of the Radium C atom, the recoil atom, is $4{\cdot}4\times10^{4}$ cm. per sec., the corresponding energy being 0·4 volt. From Blackett's ‖ work on the range of recoil atoms produced by impact with α-particles, the range of these Radium C atoms can be estimated to be between 10^{-6} cm. and 10^{-8} cm. of air at atmospheric pressure. Obstructions of this order of thickness in the form of surface films of gas and tarnishing are almost certain to be present on the plate on which the Radium B,

* Communicated by Professor Sir E. Rutherford, P.R.S.

† Phil. Mag. xix. p. 100 (1910).

‡ Phil. Mag. xxxix. p. 690 (1920).

§ Phil. Mag. xlvii. p. 23 (1924).

‖ Proc. Roy. Soc. A, ciii. p. 62 (1923).

the parent atom, is deposited say by exposure to emanation, and would consequently prevent the recoil atoms from escaping from it and being collected on a plate near by. It is evident then that special conditions will have to be realized to obtain an efficient β-ray recoil. In discussing these conditions it is not necessary to argue from a theoretical standpoint, since they can be obtained empirically from the results of previous experiments which have a bearing on the problem.

Consider in the first place experiments on α-ray recoil. Here the energy of recoil is of the order of 100,000 volts, and so whatever conditions are necessary for its detection must be realized in the case of β-ray recoil. Efficiencies up to 50 per cent. can be obtained in any case of α-ray recoil provided that the parent atom is deposited on a clean well-polished surface. (An efficiency of 100 per cent. is to be taken to mean that the maximum theoretical number of recoil atoms has been collected.) Any tarnishing of the surface causes a considerable decrease in efficiency. But in some experiments by the author on the recoil of Thorium D from Thorium C efficiencies of 100 per cent. were obtained. The Thorium C was first deposited on a nickel wire by von Lerch's method and then distilled in air from this wire on to a polished brass cylinder, from which the recoil atoms were subsequently collected in a vacuum. The first condition to be satisfied, then, to obtain an efficient β-ray recoil is that the surface of the parent atom must be prepared by distilling it on to a polished plate.

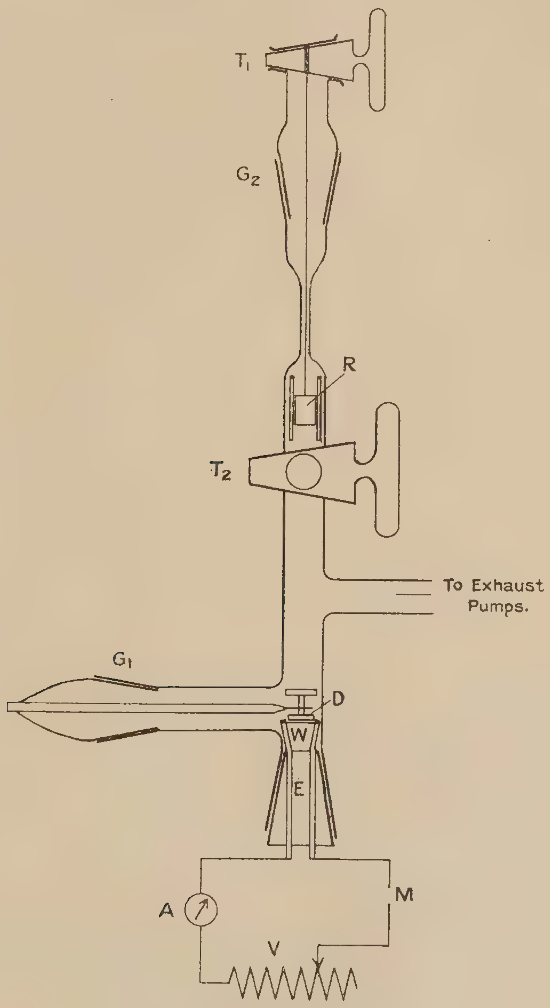
Secondly, consider the experiments on the photoelectric effect with visible radiation where the energy of the electrons is of the same order as that of the β-ray recoil atoms, about one volt. Here the escape of the electrons was greatly impeded unless a "clean" surface was used (a clean surface is one which is prepared in a vacuum and is never afterwards exposed to the atmosphere either before or during use). This will also be true of β-ray recoil atoms, and therefore the second condition to be satisfied to obtain an efficient β-ray recoil is that the parent atom must be prepared in a vacuum and never be exposed to the air before or during recoil.

The simplest way of combining these two conditions in practice is to distil the parent atom from a wire on to a plate close by in a vacuum and to collect the recoil atoms from that plate, which is not exposed to the air until the recoil is stopped. The pressure of the air should be less than 10^{-3} mm. of mercury, since at this pressure the mean free

path of the recoil atoms would be about 7 cm., and so one which has escaped from the surface of the parent atom would be certain to reach a plate a millimetre or so away.

Description of the Apparatus and Experimental Details.

Fig. 1.



General view of the apparatus.

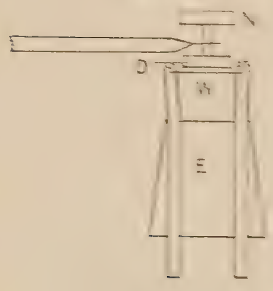
The arrangement of the apparatus is shown in figs. 1, 2, and 3. Radium Active Deposit is obtained on the platinum

wire W, and is left for 30 mins. to allow the Radium A to decay away, after which it is inserted in the apparatus so that it can be electrically heated to about 400° C., the heating current being measured by the ammeter A. The temperature, which need not be known accurately, can always be reproduced by using the same heating current.

The apparatus is exhausted by a Gaede Mercury Pump and a Charcoal Tube immersed in liquid air, a liquid-air trap being inserted between the pump and the apparatus to prevent mercury vapour from diffusing into it. A pressure of about 10^{-4} mm. of mercury was obtained, being estimated by a discharge-tube which had been calibrated by a McLeod gauge.

The wire is heated for 30 secs. to about 400° C., when some of the Radium B and C which distils off condenses on the cold disk D, a brass plate 4 mm. in diameter. The tap T_2 is closed during this distillation to prevent any Radium B and

Fig. 2.



The Cold Disc in Position for the Distillation

Fig. 3.

Cold Disc and Receiver during Recoil

C reaching the receiver R. It was necessary to use sources as large as 5 mg. of Radium B and C on the platinum wire in order to obtain recoil effects measurable on an α-ray electroscope, because a temperature of distillation of about 400° C. is the highest that can be used if the efficiency of recoil is not to be greatly decreased, and even then only a small fraction of the amount distilled is collected since the distillation is in a vacuum.

The tap T_2 is then opened, and the cold disk being turned through 180° by the ground-glass joint G_1, the receiver, a brass cylinder 4 mm. in diameter and 5 mm. long, is lowered by the windlass T_1 into the position shown in fig. 3, when a definite fraction of the recoil atoms escaping from the cold disk are collected by it. The screen N and the sleeve S prevent any Radium C recoiling from the Radium B left on the

wire or condensed on the walls of the apparatus from reaching the receiver.

The recoil is allowed to proceed for 30 mins., since it was the average value of the efficiency over 30 mins. which was required for the experiments on the half-period of Radium C. The receiver is then raised, air is let into the apparatus, and the receiver and cold disk are removed. Their activities were measured by a suitable α-ray electroscope, that of the cold disk being measured as soon as possible after removal from the apparatus and then again an hour later. The variation of the activity of the receiver was followed carefully for about 50 mins., and from the form of the curve the purity of the deposit could be estimated. Under ideal conditions only Radium C would be obtained, showing an exponential decay of half-period 19·5 mins., but in practice a small amount of Radium B is always found. This question of contamination is discussed more fully later, but it can easily be taken into account in the calculation of the efficiency of the recoil. From these measurements of the activities of the cold disk and receiver the efficiency is calculated as shown in the next paragraph.

Calculation of the Efficiency of Recoil.

The Efficiency of Recoil, ϵ, is defined by the equation

$$\epsilon = \frac{\text{No. of atoms of Radium C escaping from the cold disk by Recoil in any time.}}{\text{Half of Total No. of atoms of Radium C produced by disintegration in that time.}} \quad . \quad . \quad . \quad (1)$$

On this definition the efficiency would be 100 per cent. if the full theoretical number of recoil atoms was obtained.

To calculate the efficiency of recoil from the above measurements, we proceed as follows:—

Let B = No. of Radium B atoms on the cold disk at any time t.

C = No. of Radium C atoms on the receiver at any time t,

C_τ = No. of Radium C atoms on the receiver at time τ,

λ_2, λ_3 = Radio-active constants of Radium B and C respectively,

ω = Average solid angle subtended by the receiver over the cold disk (·4 × 2π in these experiments),

τ = Time of duration of recoil.

Then at any time t, $\frac{1}{2}\epsilon B$ atoms of Radium B are effective in producing Radium C atoms which escape from the cold disk. Also at the beginning of the recoil, $t=0$, $B=B_0$, $C=0$. A simple application of the laws of radio-active decay leads to the equation

$$C_\tau = \frac{\omega}{4\pi} \cdot \frac{\lambda_B}{\lambda_B - \lambda_C} \cdot \epsilon B_0 (e^{-\lambda_C \tau} - e^{-\lambda_B \tau}). \quad . \quad . \quad (2)$$

From this equation, knowing ω, τ, B_0, and C_τ, ϵ can be calculated.

B_0 is obtained from the measurements of the activity of the cold disk in the following way:

Let B = No. of atoms of Radium B on cold disk at any time t,

C_1 = No. of atoms of Radium C on cold disk at any time t.

At $t=0$, the beginning of the recoil, $B=B_0$, $C_1=C_0$. Then, $B=B_0 e^{-\lambda_B t}$,

$$C_1 e^{\lambda_C t} = -\frac{\lambda_B}{\lambda_B - \lambda_C} \cdot B_0 e^{-(\lambda_B - \lambda_C)t} + k,$$

where k is a constant.

From the initial condition at $t=0$, $C=C_0$, we have

$$C_1 = \frac{\lambda_B B_0}{\lambda_B - \lambda_C} \{e^{-\lambda_C t} - e^{-\lambda_B t}\} + C_0 e^{-\lambda_C t}. \quad . \quad . \quad (3)$$

Now the measured activity of the cold disk is proportional to C_1, since the ionizing effect of the β-rays from Radium B is negligible compared with that of the α-rays from Radium C. Thus, by measuring the activity of the cold disk at two times t_1 and t_2, we obtain from (3) two equations from which the two unknowns B_0 and C_0 can be calculated. In this investigation no account has been taken of the disturbing effect of the recoil on the decay, since with the small efficiencies obtained in these experiments this was found to be negligible.

C_τ is obtained by extrapolating the measured activity of the receiver to the time corresponding to the end of the recoil. In addition, it is most important to estimate the purity of the activity on the receiver for two reasons. Firstly, the only reliable criterion that the Radium C on the receiver is due to recoil is its purity. For if it is

accompanied by any appreciable quantity of Radium B (25 per cent. or more), then it is not certain that any of the Radium C present is due to recoil, for whatever caused the Radium B to reach the receiver (and it could not be β-ray recoil) might also have caused the Radium C to reach it also. Secondly, if a small amount (less than 10 per cent.) of Radium B is present, a correction must be applied to allow for the Radium C produced by it, it being certain that the rest of the Radium C present is due to recoil. This was found to be negligible in the final conditions used in the experiments, but initially a considerable amount of Radium B was always found on the receiver due to "contamination," a phenomenon well known to those working in radio-activity. If an apparatus containing a source of some few milligrammes strength is exhausted, it is found that after a few minutes minute traces of the radio-active matter on the source have spread throughout the apparatus and have condensed all over the walls. To this effect is given the name contamination. The way in which it affects the present experiments is as follows. The wire W (fig. 3) is the source from which traces of radio-active matter spread throughout the apparatus, some of it condensing on the receiver R. As the amount of Radium B on the cold disk is only about $\frac{1}{1000}$ of that on the wire, the amount of Radium C on the receiver due to contamination may easily be of the same order as that due to recoil. The presence of contamination was first discovered by testing the activity of the back of the receiver, which was found to be as great as that of the front. It is impossible to eliminate the effect, but it was found possible to get a strong enough source of Radium B on the cold disk from a parent source of given strength so as to render its effect negligible by adjusting it (the cold disk) to be as close as possible to wire W ($\frac{1}{2}$ mm.) and by increasing the time of distillation to 1 min. Under these conditions the percentage of Radium C in the activity on the receiver was always greater than 90 per cent., and in an experiment performed solely to test this point, the activity on the receiver decayed exponentially for 80 mins. with a half-period of 20·1 mins. corresponding to 95 per cent. of Radium C. From these results it is certain that the Radium C on the receiver is due to recoil and not to spurious effects such as contamination; but as it is impossible to eliminate completely the latter effects, the values of the efficiency given below should be looked upon as upper limits.

Results.

The maximum value of the efficiency of recoil obtained in these experiments was 6 per cent. The efficiency varied considerably in a way which cannot be controlled, but it was always possible to obtain 2 per cent.

The efficiency of recoil from a surface prepared as above and exposed to air for about 30 secs. was also determined, a knowledge of this being required in connexion with the work on Radium C′. The values obtained lay between 1·5 per cent. and 3 per cent. It is evident that even in this short time the "cleanness" of the surface of Radium B is impaired, thus impeding the recoil, which is just what would be expected.

One other interesting fact has emerged in the course of this work. That is, that at about 400° C. in a vacuum Radium C is more volatile than Radium B. This is in striking contrast to the volatility at atmospheric pressure, for at 600° C. Radium B distils readily, Radium C hardly at all. The difference might be due to the fact that the Radium B and C are in different states of chemical combination in air and in a vacuum.

Modification of the above Method.

Since in the above method only very small sources of Radium B are obtained, which are quite useless for the experiments on Radium C′, the following procedure was tried in the hope of getting good efficiencies but a much stronger source. The platinum wire, on which the active deposit is obtained, is inserted in the apparatus and heated in a vacuum as before. Now the temperature to which the wire is heated is adjusted so that the film of gas and other surface impurities which impede recoil are driven off (together with a little active deposit). But, on the other hand, the lowest temperature which suffices for this purpose must be used, since the heating will tend to drive some of the active deposit into the wire and so impede the recoil. The source prepared in this way will be about 1000 times as strong as that obtained by the method described above, and its surface may be equally favourable to recoil since it should approximate to a "clean" surface.

The efficiency of recoil from such a surface was measured, a few necessary modifications in the apparatus being made. The mean value obtained was 2 per cent., which compares very favourably with that obtained by the first method.

Discussion of Results.

The chief point of interest in this work is the low efficiencies obtained (6 per cent.) compared with those obtainable in the case of α-ray recoil (50–100 per cent.). It is not to be expected that such high efficiencies would be obtained for β-ray disintegration owing to the small energy of recoil, but such a large difference is rather surprising at first sight.

The following considerations may explain this difference. Firstly, the electron which causes the Radium C atom to recoil is emitted from the nucleus. Assuming that the continuous background of β-ray spectra is due to electrons from the nucleus, their velocity varies continuously over a wide range, $0{\cdot}93 \times 10^{10}$ cm. per sec. to $2{\cdot}4 \times 10^{10}$ cm. per sec. in the case of Radium B, the velocity of the recoil atoms varying from $2{\cdot}4 \times 10^{4}$ cm. per sec. to $6{\cdot}2 \times 10^{4}$ cm. per sec. and the corresponding energies being 0·1 volt and 0·6 volt. Further, these recoil velocities also correspond to temperatures of 500° A. and 3400° A. respectively. The lower temperature is much less than that required to volatilize Radium C in a vacuum, and it appears probable that an atom of Radium C with such a velocity could not escape from the surface, simply because it cannot overcome the surface forces of attraction. Consequently a certain proportion of the Radium C atoms will never escape from the Radium B surface however favourable the conditions. How great this proportion is depends upon the distribution of the number of recoil atoms (and so electrons) over the range of velocities in question and on the velocity at which escape sets in. From the work of Chadwick and Ellis * the number of electrons rises about uniformly from the minimum velocity, reaching a maximum at about $1{\cdot}7 \times 10^{10}$ cm. per sec. and falling uniformly to zero at the maximum velocity. Assuming, as is probable, that only those atoms of Radium C with a velocity greater than 5×10^{4} cm. per sec. can escape from the surface of the parent atom and be collected, it follows that more than half of them will never do so. It may be, then, that the small value of the efficiency obtained is due in part or entirely to the distribution of the velocity of the recoil atoms over a considerable range. Secondly, the diffusion of the parent atom into the plate on which it is deposited may also cause a decrease of efficiency with time in the case of a recoil as weak as this one. Such a decrease was found by Muszkat and would, assuming her results, make

* Proc. Camb. Phil. Soc. xxi. p. 274 (1923).

the average efficiency over half-an-hour about one half of the initial value.

There still remains for discussion the divergence between the value of the efficiency obtained in these experiments and those due to Muszkat. Assuming that the efficiency falls to half its initial value in 20 minutes as claimed by Muszkat, then the average efficiency over 30 minutes for a polished brass cold disk in her experiments would be 18 per cent., whereas in the present experiments only 6 per cent. was obtained. There is one factor which may explain the difference, namely contamination. She makes no mention of it in her work, and her apparatus is just as liable to it as the one described above. As she does not give the percentage purity of the Radium C obtained on the receiver, the extent to which contamination actually influenced her results cannot be estimated, but it is quite possible that this explains the difference, since values of the same order as she gives were obtained in these experiments until contamination was detected.

Summary.

An experimental determination of the efficiency of β-ray recoil of Radium C from Radium B is described.

The conditions most favourable to β-ray recoil are discussed, and to satisfy them a specially prepared surface of Radium B was used. This was obtained by distilling it from a platinum wire on to a polished brass disk, called the cold disk, in a vacuum. The recoil is then performed directly from this "clean" surface.

When the conditions had been so adjusted that contamination was negligible, the maximum efficiency obtained was 6 per cent.

A modification of the above method is described in which the sources of Radium B obtained are about 1000 times as strong as those obtained by the previous method. The efficiency obtained by this method was about 2 per cent.

It is suggested that the range of velocities of the electrons causing the recoil may be such that more than half of the recoil atoms may not have sufficient energy to escape from even a "clean" surface. This may account for the very low efficiencies obtained.

It is probable that the high value (50 per cent.) obtained by Muszkat was due to the fact that no allowance was made for contamination in her experiments.

I should like in conclusion to express my sincere thanks to Sir Ernest Rutherford, P.R.S., for suggesting this problem and for his advice and encouragement while it was being carried out, and to Mr. G. A. R. Crowe for the preparation of the Radium Active Deposit. I am indebted to the Department of Scientific and Industrial Research for a Maintenance Grant which enabled this work to be carried out.

LXXV. *The Statistical Mechanics of Assemblies of Ionized Atoms and Electrons.* By R. H. Fowler *.

§ 1. *Introduction.*—In a series of papers Prof. Darwin and the present writer have applied statistical mechanics systematically to assemblies of isolated systems, and in the last of the series have included imperfect gases †. The main object of this last extension was an attack on the properties of matter at the temperatures and densities occurring in stars. For this purpose the theory must be formulated in terms of electrons and positive nuclei, rather than in terms of the atoms and molecules of chemistry. This is easy enough, and, provided that an approach to a correct theory of assemblies of ionized atoms and electrons is possible by such refinements on the theory for perfect gases, little would remain to be done here beyond forming a descriptive catalogue of atomic constants (weights and energies) and constructing the characteristic function.

The outstanding difficulty of the desired theory lies in the well-known question of the convergence of the partition functions (*Zustandsumme*) for the stationary states of excited atoms. A simple treatment of this question has recently been suggested by Urey ‡ and Fermi §, rendering such an approach at least formally possible. On reading Urey's paper I attempted to develop his idea by generalizing it for assemblies of any sorts of atoms and ions, and electrons, with a more exact analysis of the necessary hypotheses. I came to regard a certain variant of this theory as physically preferable, though no form seemed completely convincing. This variant is described below, and compared with the original. In default of greater certainty, and in

* Communicated by the Author.

† Fowler, Proc. Camb. Phil. Soc. xxii. p. 861 (1925), with references to the earlier papers.

‡ Urey, Astrophys. Journ. lix. p. 1 (1924).

§ Fermi, *Zeit. für Phys.* xxvi. p. 54 (1924).

the belief that the differences between these and the true theory would prove to be of minor practical importance, a particular form of the theory was selected, and an extensive series of calculations for stellar interiors carried out by Mr. Guggenheim. These have since been published *.

It has been pointed out by Planck †, however, that the theory of Fermi (and its variants) is somewhat artificial, in that it ought to be possible to derive the proper form for the partition function directly and solely from the phase integral of Gibbs (with suitable quantum theory modifications). This position is of course undeniable, and Planck has given a treatment of the phase integral in this sense, based on a certain assumption. It will be necessary to examine Planck's discussion in greater detail here. The arbitrary nature of the simplifying assumption he uses becomes clear in the consideration of wider cases than he treats. His theory when generalized leads to results of very much the same form as that of Urev and Fermi. It has the real logical advantage of being directly based on the phase integral, but the arbitrary simplification it contains leaves it, I believe, almost as far from the real truth.

In spite of these admitted weaknesses, however, all forms of the theory hitherto proposed converge to give much the same results. They may therefore perhaps be accepted with some confidence for hydrogen-like atoms with one electron, for which they have been explicitly developed. They have, however, been applied by Mr. Guggenheim and myself to atoms with more electrons. We assumed in so doing that the series of stationary states of the atom or atomic ion could always be taken to be the series of stationary states revealed by the "optical" spectrum of the atom of the same structure, which can in general be referred to series of stationary states in which one or perhaps two electrons are in excited (non-normal) orbits. The existence of other possible stationary states, as shown by the X-ray levels, was of course recognized, but in the absence of an adequate basis for the construction of the whole aggregate they were omitted. The recent work, however, of Stoner ‡, Pauli §, and Heisenberg ||, amplified by Hund ¶, makes it possible to formulate this aggregate,

* Fowler & Guggenheim, Monthly Notices R.A.S. lxxxv. p. 939 (1925).

† Planck, *Ann. der Phys.* lxxv. p. 673 (1924, Dec.).

‡ Stoner, Phil. Mag. xlviii. p. 719 (1924).

§ Pauli, *Zeit. für Phys.* xxxi. p. 765 (1925).

|| Heisenberg, *Zeit. für Phys.* xxxii. p. 841 (1925).

¶ Hund, *Zeit. für Phys.* xxxiii. p. 345 (1925).

it may be crudely but at least with some show of confidence. I am inclined to believe that this is the correct basis for calculation. It makes no difference of course for low temperatures, less than 20,000° or 30,000°. But for the high temperatures of stellar interiors the results are interesting and sometimes significantly different in certain respects from the simpler theory of one excited electron.

The substance of this paper formed certain chapters of an essay submitted for the Adams Prize of 1923–24 on Statistical Mechanics with special reference to the properties of matter at stellar temperatures. This paper, however, is the result of a complete revision of the earlier work.

§ 2. *Summary of the paper.*—The contents of this paper are therefore as follows :—

In § 3 we give a formal specification of atomic dissociation theory in terms of atomic ions and free electrons on the general basis provided by statistical mechanics for assemblies of isolated systems*. In the first instance it has been assumed that the constituents behave as perfect gases with formal expressions $u(\mathrm{T})$ for their series of stationary states. This has then been amplified to include the electrostatic term of Debye and Hückel †, and corrections for the volume of each ion according to the theory (generalized) of van der Waals.

In § 4 we specify the *energies* $(\chi_r^z)_s$ of the various atoms (Z) in the various stationary states (s) of their various stages of ionization (r), and in § 5 the *weights* $(\varpi_r^z)_s$ of these states. These are required unaltered in any form of the theory.

It is becoming increasingly necessary to form a standard specification of these weights for general statistical use, which it is hoped this section will provide.

In § 6 we investigate the form of $u(\mathrm{T})$ according to the generalized theory of Urey and Fermi, and in § 7 the variant on which numerical calculations for stars have already been made. We show further how the $u(\mathrm{T})$ of these theories can be approximately summed for atoms with one or any other number of excited electrons. These summations are extended in § 8.

In § 9 Planck's suggestion is investigated and generalized, and the resulting form of $u(\mathrm{T})$ established, and in § 10 the various theories are collated. Actual applications of the theories to stellar or other problems are not undertaken here.

* Fowler, *loc. cit.*

† Debye & Hückel, *Phys. Zeit.* xxiv. pp. 185, 305 (1923).

§ 3. *The fundamental formulæ.*—We shall discuss the average state of an assembly so hot that we no longer require to recognize the existence of molecules. They can easily be included if necessary. We proceed to construct formally the characteristic function Ψ *.

As a suitable notation let

M_0^z be the (average) number of neutral atoms of atomic number Z in a volume V ;

M_r^z be the (average) number of such atoms r-times ionized ;

N be the (average) number of free electrons.

In general atoms r-times ionized must be defined to mean nuclei accompanied by $Z-r$ electrons, each of which has insufficient energy to effect an escape. That each single electron bound to a nucleus has a definite energy may be regarded as a postulate of the Quantum theory demanded by the facts of spectroscopy. The most convenient standard state of (conventionally) zero energy is that state of the assembly in which the only constituents are electrons and bare nuclei at rest at infinite separation. The bare nucleus and the electron are assumed structureless, and will have partition functions $VF_z^z(T)$ and $VG(T)$ of the usual form (p. 863). We shall use m for the mass of the electron and m^z for the bare nucleus Z. It will never be necessary to distinguish between m^z and m^z+rm $(r\leq z)$.

Consider next the normal state of each atomic ion. Let the successive ionization energies of the atom Z be $\chi_0^z, \chi_1^z, \ldots.$ χ_{z-1}^z and the weights of their normal states ϖ_r^z. Then, for the r-times ionized atom the partition function $VF_r^z(T)$ is given by

$$F_r^z(T)=\frac{(2\pi m^z kT)^{\frac{3}{2}}}{h^3}\varpi_r^z\, e^{\{\chi_r^z+\cdots+\chi_{z-1}^z\}/kT} \quad . \quad . \quad . \quad (1)$$

Each ion will in addition possess a number of excited states of greater energy content, which, on the perfect gas basis, will cause ϖ_r^z to be formally replaced by the factor $b_r^z(T)$, where

$$b_r^z(T)=\sum_{s=0}(\varpi_r^z)_s\, e^{-\{\chi_r^z-(\chi_r^z)_s\}/kT} \quad . \quad . \quad . \quad . \quad (2)$$

The state $s=0$ is the normal state of least energy and we continue to write ϖ_r^z and χ_r^z instead of $(\varpi_r^z)_0$ and $(\chi_r^z)_0$. The energy of excitation is $\chi_r^z-(\chi_r^z)_s$, so that $(\chi_r^z)_s$ corresponds to a spectral term (the sth) of the r-times ionized atom Z.

* Fowler, *loc. cit.* p. 863. Further references in this § to the same paper will be incorporated in the text with a page reference only.

When allowance is made for excluded volumes $b(T)$ is replaced by $u(T)$, where (p. 875)

$$u_r^z(\mathrm{T}) = \sum_{s=0}(\varpi_r^z)_s \exp\left[-\{\chi_r^z-(\chi_r^z)_s\}/k\mathrm{T} \right.$$
$$\left. -\{\mathrm{N}(v_r^z)_{s,\epsilon}+\Sigma_\beta \mathrm{M}_\beta(v_r^z)_{s,\beta}\}/\mathrm{V}\right]. \quad (3)$$

In equation (3) the average excluded volume for interaction with an electron is $(v_r^z)_{s,\epsilon}$ and with an atomic ion β $(v_r^z)_{s,\beta}$. The summation Σ_β is taken over all atomic types (r', s', z'). The complete form for Ψ is then (p. 875)

$$\Psi/k = \mathrm{N}\left(\log\frac{\mathrm{VG}}{\mathrm{N}}+1\right)+\Sigma_{r,z}\mathrm{M}_r^z\left(\log\frac{\mathrm{VF}_r^z}{\mathrm{M}_r^z}+1\right)$$
$$+\frac{1}{\mathrm{V}}\Sigma_{\alpha,\beta}\frac{\mathrm{M}_\alpha\mathrm{M}_\beta v_{\alpha\beta}}{\sigma_{\alpha\beta}}. \quad (4)$$

For completeness we repeat *

$$\mathrm{F}_r^z = \frac{(2\pi m^z k\mathrm{T})^{\frac{3}{2}}}{h^3}u_r^z(\mathrm{T})e^{\{\chi_r^z+\ldots+\chi_{z-1}^z\}/k\mathrm{T}}, \quad \mathrm{G} = \frac{(2\pi m k\mathrm{T})^{\frac{3}{2}}}{h^3}. \quad . \quad . \quad . \quad (5)$$

$\Sigma_{\alpha,\beta}$ is a summation over all pairs of types of massive ions and $\sigma_{\alpha\beta}=1$ $(\alpha\neq\beta)$, $\sigma_{\alpha\alpha}=2$. It is a further consequence of equations (3), (4), and (5) that (p. 876)

$$\frac{\partial\Psi}{\partial\mathrm{M}_\alpha}\equiv\frac{\partial\Psi}{\partial(\mathrm{M}_r^z)_s}=0 \quad (all\ r,s,z), \quad . \quad . \quad . \quad (6)$$

so that in any variation of N or M_r^z no explicit variation of any M_α need be made. The excluded volume corrections, when not small, are only qualitatively correct (p. 876). Further (p. 875)

$$\frac{(\mathrm{M}_r^z)_s}{(\varpi_r^z)_s\exp\left[-\{\chi_r^z-(\chi_r^z)_s\}/k\mathrm{T}-\{\mathrm{N}(v_r^z)_{s,\epsilon}+\Sigma_\beta\mathrm{M}_\beta(v_r^z)_{s,\beta}\}/\mathrm{V}\right]}$$
$$=\frac{\mathrm{M}_r^z}{u_r^z(\mathrm{T})}. \quad . \quad . \quad (7)$$

To the value of Ψ/k given by (5) we must add (a) the

* *(Added in proof)*.—In the theory of Goudsmit and Uhlenbeck (see footnote to § 5) G is greater by a factor 2.

contribution of radiation in the enclosure (p. 863) *, and (*b*) the term arising from the electrostatic charges on the massive ions and free electrons. The radiative term is properly additive. Electrostatic and excluded volume effects really interact and should be introduced together, which could probably be done by a more extensive investigation. We shall, however, be content here with the simplest form for point ions †. The complete form for Ψ is therefore

$$\Psi/k = \mathrm{N}\left(\log\frac{\mathrm{VG}}{\mathrm{N}}+1\right)+\Sigma_{r,z}\,\mathrm{M}_r^z\left\{\log\frac{\mathrm{VF}_r^z}{\mathrm{M}_r^z}+1\right\}$$
$$+\frac{1}{\mathrm{V}}\Sigma_{\alpha,\beta}\frac{\mathrm{M}_\alpha\mathrm{M}_\beta v_{\alpha\beta}}{\sigma_{\alpha\beta}}+\frac{8\pi^5k^3\mathrm{VT}^3}{45c^3h^3}+\frac{2\surd\pi\epsilon^3}{3\mathrm{V}^{\frac{1}{2}}(k\mathrm{T})^{\frac{3}{2}}}\{\mathrm{N}+\Sigma_{r,z}\,r^2\mathrm{M}_r^z\}^{\frac{3}{2}}. \quad \ldots \quad (8)$$

In conjunction with (3) and (5), (8) determines all the equilibrium properties of the assembly.

3·1. *Dissociative Equilibrium.* Submit Ψ to the variation

$$\delta\mathrm{M}_r^z=-\eta\,; \qquad \delta\mathrm{N}=\delta\mathrm{M}_{r+1}^z=\eta\,;$$

for which $\delta\Psi=0$. The $(\mathrm{M}_r^z)_s$ need not be varied explicitly. By combining (3) and (7) we can show that

$$\Sigma_{r,z}\frac{\mathrm{M}_r^z}{u_r^z}\frac{\partial u_r^z}{\partial \mathrm{N}}=-\frac{1}{\mathrm{V}}\Sigma_\beta\mathrm{M}_\beta v_{\beta,\epsilon}. \quad \ldots \quad (9)$$

With the help of (5) and (9) we find

$$\frac{\mathrm{NM}_{r+1}^z}{\mathrm{VM}_r^z}=\frac{(2\pi mk\mathrm{T})^{\frac{3}{2}}}{h^3}\frac{u_{r+1}^z(\mathrm{T})}{u_r^z(\mathrm{T})}\exp\Big[-\frac{\chi_r^z}{k\mathrm{T}}-\frac{1}{\mathrm{V}}\Sigma_\beta\mathrm{M}_\beta v_{\beta,\epsilon}$$
$$+\frac{2\surd\pi\epsilon^3(r+1)}{\mathrm{V}^{\frac{1}{2}}(k\mathrm{T})^{\frac{3}{2}}}\{\mathrm{N}+\Sigma_{r,z}\,r^2\mathrm{M}_r^z\}^{\frac{1}{2}}\Big]. \quad (10)$$

This is the generalized form of the law of mass-action, ionic volumes and charges being taken into account. It is

* For the radiation partition function, see *e.g.* Proc. Camb. Phil. Soc. xxi. p. 262 (1922).

† The validity of the numerical coefficient of the electrostatic term is more than doubtful. Eddington (M. N. vol. lxxxvi. p. 2 (1925)) has pointed out a correction which appears to reduce it by a factor about $\frac{1}{3}$. At the same time the weak point in the Debye-Hückel theory (Fowler, *loc. cit.* p. 881) may be becoming important, and it may be preferable to trust to Milner's results (Phil. Mag. xxiii. p. 551 (1912), and xxv. p. 742 (1913)). An extended re-examination is desirable.

more commonly expressed in terms of p_e, the partial pressure of the electrons, calculated as a perfect gas, when it takes the form

$$\frac{M_{r+1}^{z}}{M_r^{z}}p_e=\frac{(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3}\frac{u_{r+1}^{z}(T)}{u_r^{z}(T)}\exp\left[-\frac{\chi_r^{z}}{kT}-J+L\right], \quad (11)$$

say, where J is the extra volume term and L the extra charge term. Combined with

$$\Sigma_r\, M_r^z=M^z\ (all\ z)\ ;\quad \Sigma_{r,z}\,rM_r^z=N, \quad . \quad . \quad (12)$$

equation (10) or (11) determines the degree of ionization in the equilibrium state.

3·2. *The pressure,* $T\partial\Psi/\partial V$. We find

$$p=kT\left[\frac{N+\Sigma_{r,z}\,M_r^z}{V}+\frac{8\pi^5k^3T^3}{45c^3h^3}+\frac{1}{V^2}\left\{N\Sigma_\beta M_\beta v_{\beta,\,\epsilon}\right.\right.$$

$$\left.\left.+\Sigma_{\alpha,\,\beta}\frac{M_\alpha M_\beta v_{\alpha\beta}}{\sigma_{\alpha\beta}}\right\}-\frac{\sqrt{\pi\epsilon^3}}{3(VkT)^{\frac{3}{2}}}\left\{N+\Sigma_{r,z}\,r^2M_r^z\right\}^{\frac{3}{2}}\right],$$

$$=p_e+p_a+p_r+p_{c_1}+p_{c_2}, \quad . \quad . \quad . \quad (13)$$

say, where p_a is the partial pressure of the massive ions, p_r the radiation pressure, and p_{c_1}, p_{c_2} the correcting volume and charge terms respectively.

3·3. *The entropy.* This can be calculated directly as $\Psi+T\partial\Psi/\partial T$. The (V, T)-adiabatics of the assembly are then given directly by S=const. The resulting general expression is complicated, and to obtain the (P, V)-equation of the adiabatics, which is usually required, it is somewhat simpler to proceed by calculating directly the ratio of the specific heats.

§ 4. *The ionization energies* χ_r^z *and the energies* $(\chi_r^z)_s$ *of the stationary states.*—To use the formulæ of § 3 we must, strictly speaking, know $(\chi_r^z)_s$ for all r, s, z, that is all the spectral terms (in the widest sense) of all atoms in all stages of ionization. Such knowledge will perhaps never be available, but practical requirements are less exacting, and differ for applications to the insides and outsides of stars. For outsides of stars, to study theoretically the behaviour of a given absorption line, we require to know little more than the $(\chi_r^z)_s$ of the state from which the absorption line arises,

and the χ_r^z for the normal atom or ion, to the optical spectrum of which the line belongs. We are seldom required in such problems to consider series of stationary states in which more than one excited electron is concerned—besides the series for one electron at most a very few stationary states of the other electrons are concerned. The necessary $(\chi_r^z)_s$ and χ_r^z are known exactly as soon as the spectrum is analysed.

For the insides of stars a representative selection of elements should be sufficient. The calculations referred to have been done with O, Fe, and Ag. Here the $(\chi_r^z)_s$ are merely important in the calculation of the $u_r^z(\mathrm{T})$, in which either only the states of high excitation are relevant or else the normal state (or nearly normal states) alone. In states of high excitation of *one* electron all atoms become nearly hydrogen-like, and, arranged in suitable sequences, the $(\chi_r^z)_s$ take Rydberg's approximate form $(r+1)^2\mathrm{R}^*hc/(n-\mu)^2$. [$\mathrm{R}^*$ is Rydberg's constant, and c is the velocity of light.] It is generally sufficiently accurate to ignore the constant μ. Approximations for more than one excited electron would be less simple, but it will appear that *zero* is a sufficiently good approximation. Only the χ_r^z are left and these are wanted accurately. It must be remembered that these are the energies required to remove the electrons one after the other, leaving a normal ion at each stage. They are *not* the energies of the X-ray levels, and must always exceed these owing to the diminished screening. They may be greater by a factor as great as 5 in certain cases, and factors exceeding 2 are common.

Few values of χ_r^z are known by direct observation, but it has recently been shown by Hartree † that the majority of them can be fixed with some security by theoretical extrapolations based on our knowledge (after Bohr's theory) of the structure of atoms and spectra. The most important can be best fixed thus. Hartree has constructed tables for O, Fe, and Ag, and tables for other elements can be filled in by the same methods.

In constructing and applying these tables, a definite assumption must be made as to the normal order in which the orbits are filled up in normal ions. The order of filling up of two specified n_k orbits is (as is well known) not always the same for all nuclear charges, but is almost certainly always the same for all large enough nuclear

† Hartree, Proc. Camb. Phil. Soc. xxii. p. 464 (1924).

charges. Uncertainties of order thus only affect lightly bound orbits, are accessible to direct observation, and irrelevant in stellar interiors. It seems, however, now possible to be fairly certain of the numbers of electrons in each group or subgroup of the atom, even in the complicated structures of the Fe (and similar) transition elements *. The order assumed is the following :—

(*a*) Number of electron in order of capture.	(*b*) Type n_k of ultimate normal orbit.	(*a*) Number of electron in order of capture.	(*b*) Type n_k of ultimate normal orbit.
1	1_1	25	3_3
2	1_1	26	3_3
3	2_1	27	3_3
4	2_1	28	3_3
5	2_2	29	4_1
6	2_2	30	4_1
7	2_2	31	4_2
8	2_2	32	4_2
9	2_2	33	4_2
10	2_2	34	4_2
11	3_1	35	4_2
12	3_1	36	4_2
13	3_2	37	4_3
14	3_2	38	4_3
15	3_2	39	4_3
16	3_2	40	4_3
17	3_2	41	4_3
18	3_2	42	4_3
19 (1)	3_3	43	4_3
20 (2)	3_3	44	4_3
21	3_3	45	4_3
22	3_3	46	4_3
23	3_3	47 (3)	5_1
24	3_3	48 (3)	5_1

(1) For Z $\gtrless$ 21 (Sc) at least some 3_3 orbits must precede 4_1. From Sc to Cu there are (according to Hund) always one or two (usually two) 4_1 orbits, the electrons from 19 to Z–2 or Z–1 inclusive being bound in 3_3 orbits.

(2) For Z $\gtrless$ 22 (Ti), after Hund, and so on through this transition group.

(3) For Ag and Cd only. For large enough Z's permanent 4_4 orbits must begin at 47, but this region will not concern us.

* The number of electrons in completed sub-groups—2; 2, 2, 4; 2, 2, 4, 4, 6; etc.—are those established by the work of Stoner and Pauli (*loc. cit.*), which were first formulated by Main Smith, 'Chemistry and Atomic Structure,' 1924.

§ 5. *Weights.*—Weights are required for all stages of ionization, due account being taken of the way in which they are to be combined, and of the fact that all electrons are identical. Recent theories, particularly the work of Pauli, enable these specifications to be completed with some confidence. We start by assuming that all electrons in the atom are recognizably different and never interchanged.

All atoms and atomic ions are degenerate quantized systems. Any weight may therefore be supposed to be determined—in conformity with Bohr's postulates—by a study of the Zeeman effect in suitable magnetic fields. A "weak" magnetic field assigns, we believe, to the axis of the atom definite orientations, and the number of such different orientations must by the postulates be taken to be the *relative* weight of the normal degenerate case. Since the atom is being orientated as a whole, it does not follow at once that this is a sufficient analysis.

In the general classification of the simpler spectra, which is valid so long as the atom can be divided into a core and single series electron *, a term or state is specified by four quantum numbers n, k, j, and r, and denoted n^r_{kj}. Of these n and k have their familiar meanings of the theory of central orbits, and j and r define the moments of momentum of the whole atom and the core. The formal specifications of the spectrum are usually made in terms of numbers K, J, and R such that $K=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ for S, P, D, ... terms, $R=\frac{1}{2}, 1, \frac{3}{2}, \ldots$ for singlets, doublets, triplets, ..., and

$$|K-R|+\tfrac{1}{2}\leq J\leq K+R-\tfrac{1}{2}.$$

A very simple rule holds in all such cases. The total number of states into which n^r_{kj} splits in a weak field is 2J, and the total number of states into which a whole multiplet n^r_k splits is 4RK $[2R(2k-1)]$. The numbers 2J and 4RK are the relative weights.

The relative weights so determined must give the right ratios for any two states of the same ion, the closed groups of the core being unaltered, but the question whether the scale is always the same, so that the weights of all Zeeman components of all ions are the same, lies deeper. The recent work of Pauli, however, seems to be able to be presented so

* Or as one now says, "In scheme I" (Heisenberg, *loc. cit.*).

as to lead logically to a definite conclusion, and there is little doubt that his theory presents one aspect of the truth.

Pauli shows that a large section of spectral facts can be described by assigning to all the electrons in any ion, not members of closed groups, the whole peculiar properties of the single series electron of an alkali. The alkali spectrum is to be described thus:—The core of closed groups of electrons is isotropic without mechanical or magnetic moment. The series electron has an unmechanical duplexity (*Zweideutigkeit*) which gives rise to the (relativity) doublet form of the spectrum and so, for given k, to 4K stationary states of the outer electron in a magnetic field. These states are specified in terms of four quantum numbers n, k_1, k_2, and m_1, or n, k_1, m_1, and m_2, the latter being the suitable set for strong magnetic fields *. If we have two such series electrons, we may continue to ascribe to the core and each separate series electron the same alkali-like properties, and we obtain by combination of the $4K_1$ and $4K_2$ possible states of the two electrons not only the right number of observed terms, arrangeable in the correct groupings (weights), but also the correct magnetic energies in strong magnetic fields. We get the correct results also for more than two electrons. The argument is carried through for strong fields for which the interactions of the various electrons can be ignored. But owing to the invariance of the weights (or numbers of terms) deductions as to weights and term numbers will hold good in general.

Pauli's presentation of these facts has a valuable element of generality in that it does not directly classify the resulting terms into multiplets, for it is clear that, in complicated cases, more than one such classification may be significant. The spectrum of Ne as classified (i.) in the usual way by Paschen, (ii.) according to the new principles of Heisenberg, is an example of this †. It seems in short to be sufficiently clear that in general an atom containing,

* For convenience of reference we recall that k_1 is the azimuthal quantum number (ordinarily k) defining the mechanical nature of the central orbit, while k_2 not necessarily equal to k_1 defines the relativity effect, and m_1 (or m) the component of the atomic moment of momentum parallel to an external magnetic field. For strong fields we drop k_2 and use instead m_2 which specifies directly the extra energy in the magnetic field, and is unmechanically unequal to m_1.

† Hund, *loc. cit.*

besides closed groups, q electrons in various n_k orbits would have

$$2^{2q}K_1K_2 \dots K_q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

possible stationary states in a magnetic field. Each of these must naturally be assigned an equal weight *.

Pauli's theory could not, however, have been applied with such confidence without the beautiful subsidiary principle which he has combined with it, namely that

It is never possible for an atom to contain two or more electrons for which all four quantum numbers are the same. When one electron is present with given n, k$_1$, k$_2$, m$_1$ (*or* n, k$_1$, m$_1$, m$_2$) *that place is "engaged".*

This principle leads at once to the closing of groups and subgroups, in agreement with the specifications of Main Smith and Stoner. It accounts also in a most convincing way for the absence of particular terms—for example, of a deep triplet s-term in the alkaline earths. The number of electrons required to form a complete subgroup of a given k is equal to the number of such states, 4K. For $k=1$ the number is therefore 2. With two such electrons in orbits of the same n there is only *one* realizable possibility instead of 4, and the triplet s-term must drop out. This is true in general, and a closed group of q $(=4K)$ equivalent n_k electrons has its possible states reduced from $(4K)^q$ to 1. Viewed in this way it is at once obvious that the contribution of any closed group to the weight is always a factor unity. Similar but partial reductions occur when any two or more equivalent electrons are present although no group is thereby closed. We see too that the original assumption that cores of closed groups have always only one position in an external field is not an independent assumption but a natural consequence of Pauli's principle of exclusion. The same principle justifies us further in asserting that we can distinguish between any two electrons in the atom by the values of their four quantum numbers, even when we remove our initial assumption that the electrons themselves are recognizably distinct.

Applying Pauli's theory therefore to every electron in the atom, we can properly and systematically take the relative weight of any possible structure of the given number of elec-

* We are led of course to the same total number of terms by a repeated use of the branching principle with the successive space quantization of the electrons recently proposed by Heisenberg (*loc. cit.*). This equality of terms is fundamental to simultaneous significance of both pictures.

trons to be 2J, as fixed by the Zeeman effect, whatever the orbits of the electrons and whether or no the closed groups of the core are left untouched or broken up. When we group together all the possible multiplets arising in Heisenberg's theory from q non-equivalent electrons in given $(n_1)_{k_1}, (n_2)_{k_2}, \ldots$ orbits, the correct relative weight is given by (14) with the reductions indicated.

There remains the question of the "absolute" values of these weights compared to the weight $dp\,dq/h$ of an element of classical phase space, or compared to the weights of an atom with a different number of electrons. It has been pointed out by Bohr * that the number of states of an atom cannot be derived in the ordinary mechanical way from the product of the number of states of an ion and an electron brought into its field. The actual number is practically twice as great as one would thus calculate, in consequence of the duplexity. If we assign (say) unity as the weight of each resolved state in every atom, then the sum of the weights changes discontinuously when a free electron is bound. There is nothing thermodynamically or statistically impossible in this discontinuity, but there is a failure of *the limiting principle*, whereby the quantum theory should tend asymptotically to the classical theory for large quantum numbers. In the case in question, the partition function $\Sigma\varpi e^{-\chi/kT}$ summed over states of large quantum numbers for q electrons should tend asymptotically to

$$\frac{1}{h^{3q}}\int e^{-\chi/kT}\,dp_1\ldots dq_{3q}.$$

It is easily seen that it does not. Suppose we have an atom with q electrons all in orbits of different principal quantum number n. Then the total number of stationary states is

$$2^q\left\{\sum_1^{n_1}(2k_1-1)\right\}\left\{\sum_1^{n_2}(2k_2-1)\right\}\ldots\left\{\sum_1^{n_q}(2k_q-1)\right\} = 2^q n_1^2\ldots n_q^2. \quad (15)$$

But by comparison with the hydrogen weights $n(n+1)$ (see also § 6) the proper asymptotic form to conserve the limiting principle would lack the factor 2^q which arises from the duplexity. It seems therefore necessary to assert *that the unit of weight for any ion of* q *electrons is* $1/2^q$. This does not apply to hydrogen or hydrogen-like ions, and it seems not unreasonable that the hydrogen weights should be double those to be expected from the general rule. In an

* Bohr, *Ann. der Phys.* lxxi. p. 228 (1923), esp. p. 276.

unmechanical way they have an extra degeneracy due to the failure of the duplexity for a single electron, which cannot materialize in a purely Coulomb field *.

The foregoing count refers only to the assumption of non-interchangeable electrons. This however is exactly what we require, if, in combining weights for the whole assembly, we multiply as usual the complexions for any particular example of the assembly by

$$\frac{X!\ \Pi_z(M^z!)}{N!\ \Pi_{r,z}(M_r{}^z!)}, \quad \ldots \ldots \quad (16)$$

where X is the total number of electrons, bound or free. The factor X!/N! is the total number of permutations of all the electrons in the assembly in which a number N, unspecified in order, are free. This factor therefore allows completely for all possible permutations of the individual electrons, now no longer regarded as distinguishable, in a single atom. If we choose to regard certain of the electrons as permanently bound, they are then simply omitted from X, and are no longer counted in the possible permutations in a single atom. The same weights must be used.

In view of the preceding rules and theories we can collect together the leading results:—

(1) The weight of a single term n_{kj}^r in any spectrum of any atom with s electrons in all is $2J/2^s$.

(2) The total weight of any multiplet term n_k^r in any spectrum of any atom with s electrons in all is $4RK/2^s$.

(3)† The total weight of all terms arising from q series electrons in given n_k orbits in an atom with s electrons in all ($s-q$ in closed groups) is

$$2^q K_1 K_2 \ldots K_q / 2^{s-q}.$$

This is subject to reductions when any of the q series electrons are in orbits of the same n and k.

(4)† The total weight of all terms arising from q-series electrons in orbits of given principal quantum

* (*Note added in proof*).—It seems probable that atomic theory will shortly be rewritten in terms of the spinning electron of Goudsmit and Uhlenbeck ('Nature,' Feb. 20, 1926; *Zeit. für Phys.* vol. xxxv. p. 625 (note)). In this theory the extra factor 2 in the sum of the weights on adding a new electron arises from the structure of the electron, which has always 2 possible orientations and a weight *twice* that here assigned to it. There is an extra factor 2 in G (T), and the unit of weight for any ion of q electrons is always 1. The equations of dissociative equilibrium of this paper are mercifully unaltered.

† See also the extended form (3, 4)′ below.

numbers $n_1, n_2, \ldots$ in an atom with s electrons in all ($s-q$ in closed groups) is

$$n_1^2 \ldots n_q^2/2^{s-q}.$$

This is subject to reductions when any of the q-series electrons are in orbits of the same n.

(5) The weight of the n-quantum orbit in an atom with one electron is $n(n+1)$.

(6) These weights are to be combined together as they stand to form the weight of any complexion of any example of an assembly, the number of examples being given by (16). The weights as given have therefore been calculated with selected electrons in each orbit, no interchanges being allowed.

It is of course unnecessary to retain the 2^s factors in statistical problems involving an atom in only one stage of ionization *.

It may be useful to tabulate here the weights $\varpi_0^z (=\varpi_r^{z+r})$ of the terms of lowest energy for a number of atoms. The "weight" which is most valuable in this connexion may be

Atom.	Number of electrons in closed groups.	ϖ_0^z.	Atom.	Number of electrons in closed groups.	ϖ_0^z.
1 H	0	2	19	18	$10/2^{19}$
2 He	2	$1/2^2$	20	18	$45/2^{20}$
3 Li	2	$2/2^3$	21	18	$120/2^{21}$
4 Be	4	$1/2^4$	22	18	$183/2^{22}$
5 B	4	$6/2^5$	23	18	$250/2^{23}$
6 C	4	$15/2^6$	24	18	$183/2^{24}$
7 N	4	$20/2^7$	25	18	$120/2^{25}$
8 O	4	$15/2^8$	26	18	$45/2^{26}$
9 F	4	$6/2^9$	27	18	$10/2^{27}$
10 Ne	10	$1/2^{10}$	28	28	$1/2^{28}$
11 Na	10	$2/2^{11}$	29	28	$2/2^{29}$
12 Mg	12	$1/2^{12}$	30	30	$1/2^{30}$
13 Al	12	$6/2^{13}$	31	30	$6/2^{31}$
14 Si	12	$15/2^{14}$	32	30	$15/2^{32}$
15 P	12	$20/2^{15}$	33	30	$20/2^{33}$
16 S	12	$15/2^{16}$	34	30	$15/2^{34}$
17 Cl	12	$6/2^{17}$	35	30	$6/2^{35}$
18 A	18	$1/2^{18}$	36	36	$1/2^{36}$

* (*Note added in proof*).—In the theory of Goudsmit and Uhlenbeck these factors 2^s do not occur, and the weight of the n-quantum orbit in an atom with one electron is $2n^2$. Hydrogen-like atoms are no longer apparent exceptions.

taken to be the sum of the weights of all terms in which all the electrons are in orbits of the proper (least possible) values of n and k. In the case of atoms after A, 18, we give the values suitable for large core charges, the 3_3 orbits being next added according to the scheme of § 4. The values for Nos. 3–10, repeated for 11–18 and 29–36, are from Pauli; the values for 19–28 from Hund.

It will be necessary in applications to be able to divide up the electrons in any ion into those in their normal or nearly normal orbits—orbits of normal n and k—and those in orbits of high excitation. This division will not necessarily be the same as a division into electrons in closed groups or subgroups and the rest, though these divisions will most frequently agree. The foregoing rules refer explicitly to a division into closed groups and other electrons, but they can easily be reformulated. In rules (3) and (4) above the factor $1/2^{s-q}$ is really the weight of the atomic core of closed groups. When the core of $s-q$ electrons is not entirely composed of closed groups, we have merely to substitute the weight $\varpi_0{}^{s-q}$ from the foregoing table for $1/2^{s-q}$. Rules (3) and (4) then read:

(3, 4)′ The total weight of all terms arising from q series electrons in orbits of given n_k (given n) in an atom with s electrons in all is

$$2^q \mathrm{K}_1 \mathrm{K}_2 \ldots \mathrm{K}_q \varpi_0{}^{s-q} \quad (n_1{}^2 \ldots n_q{}^2 \varpi_0{}^{s-q}).$$

This is subject to reductions when any of the q series electrons are in orbits of the same n_k (same n)*.

§ 6. *The Theory of Urey and Fermi.*—In this theory the atoms and ions are assigned an actual volume equal to that of a sphere whose radius is the semi-axis major of the orbit of the electron. Hitherto it has been formulated for hydrogen only. The formulæ of § 3 are at once applicable, determine u (T), and lend themselves to generalization. The excluded volumes of equation (3) are then spheres whose radius is the sum of the radii of the two interacting types. In the approximations of Urey and Fermi the radius of the interacting system (β) is neglected compared to the radius of the (r, s, z)-ion itself. This will introduce no error at low temperatures in the cases they discuss in which highly

* (*Added in proof*).—In the theory of Goudsmit and Uhlenbeck these formulæ become $2^{2q} k_1 k_2 \ldots . k_q \varpi_0{}^{s-q}$, $2^q n_1{}^2 \ldots . n_q{}^2 \varpi_0{}^{s-q}$.

excited orbits are rare. As a result we obtain from (3) for hydrogen:

$$u(\mathrm{T}) = \Sigma_t t(t+1) \exp\left\{ -\frac{\chi}{k\mathrm{T}}\left(1-\frac{1}{t^2}\right)-\alpha t^6 \right\}, \quad . \quad (17)$$

where

$$\alpha = \frac{4\pi}{3}\frac{\mathrm{N}+\Sigma_\beta \mathrm{M}_\beta}{\mathrm{V}}a^3 = \frac{4\pi}{3}\frac{p_e+p_a}{k\mathrm{T}}a^3. \quad . \quad . \quad (18)$$

In (18) a is the radius of the 1-quantum orbit in hydrogen, $5{\cdot}34\times10^{-9}$ cm., and χ its ionization energy, 13·54 volts. More generally at high temperatures a better approximation to (3) is obviously provided by replacing t^6 by $(t_0^2+t^2)^3$, where at_0^2 is the average radius of all the interacting systems. This improvement will not affect orders of magnitude and we shall not investigate it in detail.

To formulate the theory for any atom with one excited electron we have obviously only to replace αt^6 by $\alpha n_t^6/(r+1)^3$ and $t(t+1)$ by ϖ_t, where n_t is the effective quantum number and ϖ_t the weight of the tth orbit and $r+1$ is the core charge. For an atom with any number of excited electrons we have presumably to replace n_t by $(n_{\max.})_t$, denoting thereby the greatest effective quantum number among the excited electrons in the tth state. In general we can expect to be able to arrange the states of any atom into series in which the quantum defect is roughly constant, and the effective quantum number increases by unity from term to term. This of course can be done with great exactness for atoms with a single excited electron. In general the quantum defect may vary considerably with the k of the greatest orbit, and with variations in any of the quantum numbers of the other excited orbits, but as a first approximation it will be legitimate to ignore these variations and group together all the terms in $u(\mathrm{T})$ which have a given principal quantum number for the greatest orbit. We can then write

$$u(\mathrm{T}) = \Sigma_\tau\left(\Sigma'_t \varpi_t e^{-\{\chi-\chi_t\}/k\mathrm{T}}\right)e^{-\alpha n_\tau^6/(r+1)^3}, \quad . \quad . \quad (19)$$

where Σ' is summed over all states in which the principal quantum numbers of every electron are less than or equal to τ, and one at least is equal to τ.

To elucidate (19) further we must group together the terms that belong to given numbers of highly excited electrons. Suppose there are q of these, and s electrons in all. Then for these states we can ignore χ_t and take χ to be effectively $\chi+\ldots+\chi_{r+q-1}$, the energy required to

remove entirely the q (highly excited) electrons from their normal orbits. Thus these states contribute to $u(\mathrm{T})$

$$e^{-\{\chi_r+\dots+\chi_{r+q-1}\}/k\mathrm{T}}\Sigma_\tau(\Sigma_t{}'\varpi_t)\,e^{-\alpha n_\tau{}^6/(r+1)^3}.$$

If we ignore reductions for equivalent orbits which do not affect the term of highest order, we find by (15) and the rules of § 5 that, summed over all states with all q principal quantum numbers less than or equal to τ,

$$\Sigma_t\,\varpi_t = \varpi_0{}^{s-q}\Sigma_{t_1,t_2,\dots,t_q\leq\tau}t_1{}^2t_2{}^2\dots t_q{}^2 \backsim \frac{\varpi_0{}^{s-q}}{3^q}\tau^{3q}.$$

Therefore, by differentiation,

$$\Sigma_t{}'\varpi_t \backsim \frac{3q\varpi_0{}^{s-q}}{3^q}\tau^{3q-1}. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Hence these states contribute to $u(\mathrm{T})$

$$\frac{3q\varpi_0{}^{s-q}}{3^q}\,e^{-\{\chi_r+\dots+\chi_{r+q-1}\}/k\mathrm{T}}\Sigma_\tau\tau^{3q-1}\,e^{-\alpha n_\tau{}^6/(r+1)^3}.$$

In this summation for a first approximation we shall omit the quantum defect and replace the sum by the integral

$$\int_0^\infty \tau^{3q-1}e^{-\alpha\tau^6/(r+1)^3}d\tau,$$

or

$$\tfrac{1}{6}\Gamma(\tfrac{1}{2}q)\left\{\frac{(r+1)^3}{\alpha}\right\}^{\frac{1}{2}q}.$$

The contribution to $u(\mathrm{T})$ is therefore

$$\Gamma(1+\tfrac{1}{2}q)\varpi_0{}^{s-q}\left\{\frac{(r+1)^3}{9\alpha}\right\}^{\frac{1}{2}q}e^{-\{\chi_r+\dots+\chi_{r+q-1}\}/k\mathrm{T}}. \quad (21)$$

There is a similar contribution for every possible value of q; the contribution for $q=0$ (no highly excited orbits) is just $\varpi_0{}^s$ the weight of the normal and effectively normal states. The complete result may be written, in the usual notation of this paper,

$$u_r{}^z(\mathrm{T}) = \varpi_r{}^z + \sum_{q=1}^{q=z-r}\Gamma(1+\tfrac{1}{2}q)\varpi_{r+q}{}^z\left\{\frac{(r+1)^3}{9\alpha}\right\}^{\frac{1}{2}q}$$
$$\times\,e^{-\{\chi_r{}^z+\dots+\chi_{r+q-1}^z\}/k\mathrm{T}}. \quad (22)$$

In general it will be found that one term in (22) is dominant for given values of the density and temperature.

In such a case nearly all the atoms M_r^z present will have just q highly excited electrons, and the rest in normal orbits, generally forming closed groups. If there is at most a single excited electron ($q=1$), then

$$u_r^z(\mathrm{T}) = \varpi_r^z + \frac{\sqrt{\pi}\,\varpi_{r+1}^z}{2}\left\{\frac{(r+1)^3}{9\alpha}\right\}^{\frac{1}{2}} e^{-\chi_r^z/k\mathrm{T}}. \quad . \quad (23)$$

This is the simplest generalization of the theory of Urey and Fermi. They do not however appear to have noticed the possibility of these simple approximate summations, whose accuracy is ample for most applications.

§ 7. *Variants of the foregoing theory.*—Different methods can be proposed for estimating the excluded volumes. We will expound shortly a variant which has been used for systematic astrophysical work *, in order to put on record the basis of those calculations. It cannot be claimed to be ultimately correct, so it may be shortly treated, but it seems probable that it does contain a valuable element of the final theory in that it makes the excluded volumes tend to zero as $\mathrm{T}\to\infty$. We return to this point later.

Urey and Fermi, in their theory, assume in effect that in the ordinary processes of an assembly in statistical equilibrium the electronic orbits of two distinct atoms cannot in general inter-penetrate. When these orbits are the quickly traversed space-filling orbits of a normal atom we have every reason to believe in this (perhaps non-mechanical) impenetrability, which gives to atoms and matter in general its familiar property of extension. At first sight it is hardly physically convincing to postulate this property for the large nearly degenerate orbits of highly excited atoms. But it may be argued that the only necessary part of this assumption is :—The orbits of the electrons of two distinct atoms, or of an atom and a free electron, never interpenetrate in a collision which fails to change the quantum state of one atom at least. In counting complexions we consistently ignore all processes of exchange, being content with the mere possibility of their occurrence. For the purpose of determining the equilibrium state, the excluded volume of any pair of systems is that region of space into which on the average the other system may not come without causing a change of quantum state. Such an argument may perhaps be held to give some physical reality to the theory of Urey and Fermi. It suggests an alternative method of estimating such excluded volumes.

* Fowler and Guggenheim, *loc. cit.*

As a possible improvement on the original form, the above analysis suggests that the excluded volumes should be calculated directly from the target areas for transference and ionization by inelastic (and superelastic) collisions according to the ionization theory of Sir J. J. Thomson. These collisions of course in themselves would preserve the perfect gas laws. It is only suggested that the frequency of these collisions indicates the order of the excluded volumes according to their analysis in this section. We need not give details. If $S_1^2(\zeta)$ represents the target area for a given atom for a successful inelastic impact by a ζ-electron, requiring an expenditure ζ_{12} of energy, then the average target area for all electronic encounters can be shown to be

$$S_1^{2*}=\frac{e^{-\zeta_{12}/kT}}{(kT)^2}\int_0^\infty e^{-\eta/kT}(\zeta_{12}+\eta)S_1^2(\zeta_{12}+\eta)\,d\eta. \qquad (24)$$

According to Thomson's theory,

$$S_1^2(\zeta)=\frac{\pi\epsilon^4}{\zeta}\left(\frac{1}{\zeta_{12}}-\frac{1}{\zeta}\right),$$

from which we find

$$S_1^{2*}\backsim\frac{\pi\epsilon^4}{kT\zeta_{12}}\quad\left(\frac{\zeta_{12}}{kT}\ small\right). \quad . \quad . \quad . \qquad (25)$$

We now take S_1^{2*} to be πR^2, where for the moment R is the radius of the quasi-excluded volume $v_{\alpha,\epsilon}$, in which a mean has been taken for all electrons. It follows that

$$v_{\alpha,\epsilon}\backsim\frac{4\pi}{3}\frac{\epsilon^6}{(kT\zeta_{12})^{\frac{3}{2}}}. \quad . \quad . \quad . \quad . \quad . \qquad (26)$$

If we calculate $\overline{R^3}$ or $\overline{(S_1^2)^{\frac{3}{2}}}$ instead of $\overline{S_1^2}$, we get the same result, with an extra factor $\sqrt{\pi}$, which is not of serious importance. The energy values of a sequence of optical terms behave like

$$(r+1)^2R^*hc/(n-\mu)^2,$$

so that when n is large one may take ζ_{12} to be given by

$$\zeta_{12}\backsim 2(r+1)^2R^*hc/(n-\mu)^3,$$

and therefore

$$v_{\alpha,\epsilon}\backsim\frac{4\pi}{3}\frac{\epsilon^6(n-\mu)^{\frac{9}{2}}}{\{2(r+1)^2R^*hckT\}^{\frac{3}{2}}}. \quad . \quad . \quad . \qquad (27)$$

A similar investigation can be given for the excluded

volume for massive ions, which at sufficiently high temperatures will be dominant owing to their greater charge and smaller speed. We shall not give details here, as, for simplicity, the actual calculations were made without taking these into account.

With a single excited electron, a set of optical states of maximum multiplicity 2R contributes to $u_r^z(\mathrm{T})$

$$\frac{1}{2^{z-r}}\Sigma_{\mathrm{K},n}4\mathrm{RK}\exp\left[-\{\chi_r^z-(\chi_r^z)_{\mathrm{K},n}\}/k\mathrm{T}-b_r(n-\mu_\mathrm{K})^{\frac{9}{2}}\right],$$

where
$$b_r=\frac{\mathrm{N}}{\mathrm{V}}\frac{4\pi}{3}\frac{\epsilon^6}{\{2(r+1)^2\mathrm{R}^*hck\mathrm{T}\}^{\frac{3}{2}}}.$$

The resulting summation after the manner of § 6 leads finally to the expression

$$u_r^z(\mathrm{T})=\varpi_r^z+\frac{1}{2^{z-r}}\left(\Sigma_\mathrm{R}2\mathrm{R}\right)e^{-\chi_r^z/k\mathrm{T}}\tfrac{1}{3}\Gamma(1+\tfrac{2}{3})b_r^{-\frac{2}{9}} \qquad (28)$$

The expression $\Sigma_\mathrm{R}2\mathrm{R}/2^{z-r}$ is equivalent to ϖ_{r+1}^z at least in simple cases.

A possible correction for the terms $(\chi_r^z)_{\mathrm{K},n}$ can be investigated. It leads approximately to an extra factor

$$\exp\left\{\frac{(r+1)^2\mathrm{R}^*hc}{k\mathrm{T}}\left(\frac{4}{9b_r}\right)^{-4/9}\right\}$$

in the second term. This proves to be always so nearly unity that it can be ignored in view of other uncertainties; a similar investigation justifies the neglect of χ_t in § 6.

The calculations mentioned were made using (28) on the assumption of just one excited electron, with an estimated value of $\Sigma_\mathrm{R}(2\mathrm{R})$ for all known optical terms, but with standard weights unity instead of $1/2^{z-r}$.

This theory extends very simply to atoms with more than one excited electron. One may presume that each electron has its own excluded volume, in general independent of all the others. This being so, the complete value of $u(\mathrm{T})$ would be formed by the continued product of expressions like (28), one for each electron, with a maximum multiplicity 2 for each.

§ 8. *Other mean values for excited atoms.*—It is possible to calculate such other mean values derived from $u(\mathrm{T})$ as may be required by the same process. For example, the average

energy content of any type of atom is given by the standard formula

$$kT^2 \frac{\partial}{\partial T} \log u(T),$$

in which of course only the factors $(\chi - \chi_t)/kT$ are differentiated. This involves the computation of $u'(T)$ or, what is the same thing, $\overline{(\chi - \chi_t)}$. It is at once obvious that if the normal terms predominate $\overline{(\chi-\chi_t)}=0$, and if the highly excited terms predominate $\overline{(\chi-\chi_t)}=\chi$. More precisely (22) yields the equation

$$\frac{du_r^z(T)}{dT} = \sum_{q=1}^{q=z-r} (\chi_r^z + \ldots + \chi_{r+q-1}^z) \frac{\Gamma(1+\frac{1}{2}q)}{2^{z-r-q}} \left\{ \frac{(r+1)^5}{9\alpha} \right\}^{\frac{1}{2}q} \times e^{-\{\chi_r^z + \ldots + \chi_{r+q-1}^z\}/kT} ; \quad (29)$$

when the term $q=q^*$ is predominant in (29) and so also in (22) we have

$$kT^2 \frac{\partial}{\partial T} \log u_r^z(T) = \chi_r^z + \ldots + \chi_{r+q^*-1}^z . \quad . \quad . \quad (30)$$

The energy content is the same as if these q^* electrons were free and *at rest* relative to the ion. Similar conclusions follow for (23) and (28).

Other expressions which occur in the general formulæ are

$$\frac{1}{V} \Sigma_\beta M_\beta v_{\beta,\epsilon}, \quad \frac{1}{V^2} \left[N \Sigma_\beta M_\beta v_{\beta,\epsilon} + \Sigma_{\alpha,\beta} \frac{M_\alpha M_\beta v_{\alpha,\beta}}{\sigma_{\alpha,\beta}} \right].$$

These, from their formation by equations (9) and $p = T\partial\Psi/\partial V$, can be evaluated as

$$-\Sigma_{r,z} M_r^z \frac{\partial}{\partial N} \log u_r^z, \quad \tfrac{1}{2}\Sigma_{r,z} M_r^z \left(\frac{\partial}{\partial V} - \frac{N}{V}\frac{\partial}{\partial N} \right) \log u_r^z, \quad (31)$$

respectively. In actual applications they are naturally calculated from the summations for the u_r^z.

The summed form of u_r^z is given by (22), but it is hardly necessary, for the accuracy suitable to this part of the theory, to retain more than the dominant term $q=q^*$ in (22). To this approximation,

$$\frac{\partial}{\partial N} \log u_r^z = -\tfrac{1}{2}q^* \frac{\partial}{\partial N} \log \alpha = -\frac{\frac{1}{2}q^*}{N + \Sigma_\beta M_\beta}, \quad . \quad . \quad (32)$$

$$\left(\frac{\partial}{\partial V} - \frac{N}{V}\frac{\partial}{\partial N} \right) \log u_r^z = \frac{\frac{1}{2}q^*}{V} \frac{2N + \Sigma_\beta M_\beta}{N + \Sigma_\beta M_\beta} . \quad . \quad (33)$$

In general q^* the average number of bound but highly excited electrons will vary with r and z and must be written $(q_r^z)^*$. We then find

$$\frac{1}{V}\Sigma_\beta M_\beta v_{\beta,\epsilon} = \frac{1}{2}\frac{\Sigma_{r,z}(q_r^z)^* M_r^z}{N+\Sigma_\beta M_\beta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$\frac{1}{V^2}\left[N\Sigma_\beta M_\beta v_{\beta,\epsilon} + \Sigma_{\alpha,\beta}\frac{M_\alpha M_\beta v_{\alpha,\beta}}{\sigma_{\alpha,\beta}}\right] = \frac{\Sigma_{r,z}(q_r^z)^* M_r^z}{2V}\cdot\frac{N+\frac{1}{2}\Sigma_\beta M_\beta}{N+\Sigma_\beta M_\beta} \quad . \quad (35)$$

In the variant of the theory described in § 7 there is only one excited electron, $v_{\alpha,\beta}=0$ and $v_{\beta,\epsilon}$ has a different law of variation with quantum number, so that $\frac{1}{2}(q_r^z)^*$ is replaced by $\frac{2}{3}$ and all the terms in $\Sigma_\beta M_\beta$ disappear from (34) and (35). The excluded volume corrections are then very easily estimated both for dissociative equilibrium and for pressure. For the former (34) shows that the extra factor e^{-J} in (11) is such that J is equal to two-thirds of the ratio of number of massive ions to number of free electrons. This is a number of the order 1/30 in stellar interiors and of no importance. For the latter (35) shows an extra term in pV/kT equal to two-thirds the number of massive ions; this again is only a small correction which is studied in detail in the papers quoted †.

In any form of the generalized theory with any number of highly excited electrons equations (34) and (35) serve to determine these corrections quite simply. They are larger than the corrections for one excited electron, but still not of very great importance in stellar work.

The methods of this section for calculating these corrections can of course be used as soon as $u_r^z(T)$ has been summed, whatever approximations may have been used in this summation, whether those of § 6, neglecting t_0^2, or not.

§ 9. *Planck's Theory.*—In an attempt to avoid the arbitrary element in Fermi's theory, Planck ‡ has returned to the Gibbsian phase integral for a mixture of electrons and nuclei, and has approached the problem by direct calculation instead of by attempting to patch up the perfect gas theory. It is still doubtful, in my opinion, whether the

† Fowler and Guggenheim, *loc. cit.*
‡ *Loc. cit.*

correct deductions can be drawn in any simple way, but fundamentally the method of approach must be correct. It will be necessary to discuss and generalize Planck's calculations here. We will start by briefly restating his theory for massive point charges $+Z\epsilon$ and free and bound electrons, assuming for simplicity at this stage that at most one electron per nucleus is bound.

The classical phase integral for a single movable electron and fixed nucleus is

$$F = \frac{1}{h^3} \iiiint e^{-\eta/kT} p^2\, dp\, d\Omega_p r^2\, dr\, d\Omega_r, \quad . \quad . \quad . \quad (36)$$

where

$$\eta = \frac{1}{2m} p^2 - \frac{Z\epsilon^2}{r}. \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Ω_p and Ω_r are elements of solid angle defining the directions of the momentum and position vectors. Thus F can be written:

$$F = \frac{\surd(2m^3)}{h^3} \iiiint e^{-\eta/kT} (\eta r^2 + Z\epsilon^2 r)^{\frac{1}{2}} r\, dr\, d\eta\, d\Omega_r\, d\Omega_q.$$

Let V, the volume available to the electron, be a sphere of radius A, and suppose that an η' can be chosen so that

$$Z\epsilon^2/A \ll \eta' \ll kT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

Then the contributions to F can be divided into three parts:—

(1) F_1. $\infty > \eta > 0$. Dissociated. Classical.

(2) F_2. $0 > \eta > -\eta'$. Combined. Effectively Classical.

(3) F_3. $-\eta' > \eta > -\infty$. Combined. Quantized.

In (3) the phase integral must be replaced by a summation over the possible stationary states.

(1) In F_1 we have $\eta \gg Z\epsilon^2/r$ over practically the whole of the effective domain of integration. Hence we replace the factor $(\eta r^2 + Z\epsilon^2 r)^{\frac{1}{2}}$ by $\eta^{\frac{1}{2}} r$, and find

$$F_1 = \frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

which is the ordinary partition function for the free electron.

(2) In F_2 we have effectively $\eta/kT = 0$. Putting $\alpha = -\eta$, we find

$$F_2 = \frac{16\pi^2 \surd(2m^3)}{h^3} \int_0^{\eta'} d\alpha \int_0^{a} (Z\epsilon^2 r - \alpha r^2)^{\frac{1}{2}} r\, dr, \quad . \quad (39)$$

where a is the smaller of $Z\epsilon^2/\alpha$ and A.

(3) In F_3 we have to replace the phase integral by the quantum sum :

$$F_3 = \sum_1^{n'} n(n+1)e^{-\chi_n/kT} \quad (\chi_n = R^* hcZ^2/n^2), \quad . \quad . \quad (40)$$

where

$$n' = (R^* hcZ^2/\eta')^{\frac{1}{2}}.$$

Thus far Planck. He points out further that under assumption (I.) $F_2 \ll F_1$, and argues that F_2 can therefore be neglected. It does not appear to me that this is logical. It seems rather that the condition for neglecting F_2 is $F_2 \ll F_3$, and this is *not* guaranteed by (I.). It appears to me necessary (or at the least preferable) to calculate F_2 exactly (this is easy) and to use $F_2 + F_3$ as the contribution from the bound orbits of the electron. In F_2 put $r = (Z\epsilon^2/\alpha)\sin^2\phi$. Then

$$F_2 = \frac{32\pi^2\sqrt{(2m^3)}}{h^3}(Z\epsilon^2)^3 \int_0^{\eta'} \frac{d\alpha}{\alpha^{\frac{5}{2}}} \int_0^{a} \sin^4\phi \cos^2\phi \, d\phi,$$

where a is $\arcsin(\alpha A/Z\epsilon^2)^{\frac{1}{2}}$, if this is real, or else $\frac{1}{2}\pi$. The double integral therefore divides into

$$\int_0^{Z\epsilon^2/A} \frac{d\alpha}{\alpha^{\frac{5}{2}}} \int_0^{\arcsin(\alpha A/Z\epsilon^2)^{\frac{1}{2}}} \sin^4\phi \cos^2\phi \, d\phi + \int_{Z\epsilon^2/A}^{\eta'} \frac{\pi}{32} \frac{d\alpha}{\alpha^{\frac{5}{2}}}$$

or

$$\frac{2}{(Z\epsilon^2/A)^{\frac{3}{2}}} \int_0^{\frac{1}{2}\pi} \frac{\cos\theta \, d\theta}{\sin^4\theta} \int_0^{\theta} \sin^4\phi \cos^2\phi \, d\phi + \frac{\pi}{32}\int_{Z\epsilon^2/A}^{\eta'} \frac{d\alpha}{\alpha^{\frac{5}{2}}}.$$

The last double integral can be evaluated by integration by parts. It is

$$-\frac{1}{3}\int_0^{\frac{1}{2}\pi} \sin^4\phi \cos^2\phi \, d\phi + \frac{1}{3}\int_0^{\frac{1}{2}\pi} \frac{d\theta}{\sin^3\theta} \sin^4\theta \cos^2\theta = \frac{1}{9} - \frac{\pi}{96}.$$

Thus

$$F_2 = \frac{32\pi^2\sqrt{(2m^3)}(Z\epsilon^2)^3}{h^3}\left[\frac{2}{9}\frac{A^{\frac{3}{2}}}{(Z\epsilon^2)^{\frac{3}{2}}} - \frac{\pi}{48}\frac{1}{(\eta')^{\frac{3}{2}}}\right],$$

$$= Z^3(R^* hc)^{\frac{3}{2}}\left[\frac{32}{9\pi}\frac{A^{\frac{3}{2}}}{(Z\epsilon^2)^{\frac{3}{2}}} - \frac{1}{3}\frac{1}{(\eta')^{\frac{3}{2}}}\right]. \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Now by the arguments of former sections we have approximately

$$F_3 = 2e^{\chi_1/kT} + \tfrac{1}{3}n'^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Therefore combining (41) and (42) we have

$$e^{\chi_1/kT}u(T) = F_2 + F_3 = 2e^{\chi_1/kT} + \frac{32}{9\pi}\frac{(ZR^*hcA)^{\frac{3}{2}}}{\epsilon^3}. \quad . \quad (43)$$

This is the partition function for the one bound electron. The second term will generally be dominant for large T, in which case Planck's discussion seems inadequate.

When the assembly contains a number of fixed nuclei and one electron, F is still given by (36) with

$$\eta = \frac{1}{2m}p^2 - \Sigma_a \frac{Z\epsilon^2}{r_a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

The electron can only be *bound* to one nucleus at a time, and the suggestion made by Planck is equivalent to asserting that *when* $\eta < 0$ *the electron is bound to the nearest nucleus.* Each nucleus then makes a contribution like (43) to F, which may be described by saying that each nucleus has this partition function for a bound electron, if A is so chosen that on the average the bound electron is nearer to the selected nucleus than to any other. If there are M nuclei we must therefore take

$$M \,.\, \tfrac{4}{3}\pi A^3 = V. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

The essential part of (I.) is then the condition

$$Z\epsilon^2\left(\frac{M}{V}\right)^{\frac{1}{3}} \leqslant kT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II.)$$

Planck's suggestion can now be generalized for a number of nuclei of different positive charges. The condition that the electron should be bound to nucleus 1 rather than to nucleus 2 is now naturally

$$Z_1/r_1 > Z_2/r_2.$$

This means that to each nucleus (Z) we must now attach a mean volume proportional to Z^3. If we now define a radius A by the equation

$$\tfrac{4}{3}\pi A^3\, \Sigma_z Z^3 M^z = V \quad . \quad . \quad . \quad . \quad (46)$$

then the actual radius A_1 for use in (43) for a nucleus Z_1 will be

$$A_1^3 = \frac{3}{4\pi}\frac{Z_1^3 V}{\Sigma_z Z^3 M^z}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

The partition function for the nucleus Z_1 in general may

therefore be written

$$F_2+F_3 = 2e^{\chi_1/kT}+\left[\frac{32}{9\pi}\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}\frac{(R^*hc)^{\frac{3}{2}}}{\epsilon^3}\right]\frac{Z_1{}^3V^{\frac{1}{2}}}{(\Sigma_z Z^3M^z)^{\frac{1}{2}}}. \quad (48)$$

The value of the permanent constant in [ ], to be written B, is $5{\cdot}086\times10^{11}$.

On the rest of Planck's development allowing of more than one electron and moving nuclei it is not necessary to comment here, so long as we do not allow any one nucleus to capture more than one electron, and are prepared to ignore the effect of this movement on the rule for fixing the particular nucleus to which an electron is bound. In our notation therefore

$$u^{z_1}_{z_1-1}(T) = 2+B\frac{Z_1{}^3V^{\frac{1}{2}}}{(\Sigma_z Z^3M^z)^{\frac{1}{2}}}e^{-\chi^{z_1}_{z_1-1}/kT}. \quad . \quad . \quad (49)$$

To extend the argument to the capture of more than one electron is not difficult, provided rather rough approximations are allowed. We shall obviously approximate fairly closely to the catching power of an atomic ion for its tth electron by assuming that it captures like a point charge $(Z-t+1)\epsilon$. This will of course be close to the truth when the previously caught electrons are in orbits of less excitation than the tth. In general it must *underestimate* the efficiency of the ion for capture of the next electron. An *overestimate* of the efficiency can be made by assuming that the ion captures like a point charge $(Z-t')\epsilon$, where t' is the number of electrons practically always in normal orbits (usually closed groups). In many applications these two limits will not be widely different, but the former may be expected to be the better approximation. With the weights laid down in § 5 the two parts F_2 and F_3 fit together as before for each stage of capture.

In order to estimate the value of $u_r^z(T)$ we proceed as in § 6 and consider separately the parts arising for various specified numbers q of highly excited electrons. When there are no highly excited electrons the weight of the normal state is no longer 2 but ϖ_r^z. When there are q highly excited electrons the weight of the remaining core is no longer unity but ϖ^z_{r+q}. Under the assumptions we have made, ignoring reductions for equivalent orbits, the contribution for q such electrons will be equal to the continued product of the contributions for each of the q electrons in order, with an extra factor ϖ^z_{r+q} for the weight of the core. According therefore

to the assumed catching power of the ion we find the following forms for $u_r^z(\mathrm{T})$:—

$$u_r^z(\mathrm{T}) = \varpi_r^z + \sum_{q=1}^{q=z-r} \varpi_{r+q}^z (r+1)^{3q}\mathrm{B}^q \left\{ \frac{\mathrm{V}}{\Sigma_{r,z}(r+1)^3\mathrm{M}_r^z} \right\}^{\frac{1}{2}q} \times e^{-\{\chi_r^z+\ldots+\chi_{r+q-1}^z\}/k\mathrm{T}}, \quad (50\,a)$$

$$u_r^z(\mathrm{T}) = \varpi_r^z + \sum_{q=1}^{z-r} \varpi_{r+q}^z (r+1)^{3q}\mathrm{B}^q \left\{ \frac{\mathrm{V}}{\Sigma_{r,z,q}(r+q)^3(\mathrm{M}_r^z)_q} \right\}^{\frac{1}{2}q} \times e^{-\{\chi_r^z+\ldots+\chi_{r+q-1}^z\}/k\mathrm{T}}. \quad (50\,b)$$

In (50 b) $(\mathrm{M}^z)_q$ is the average number of atomic ions of atomic number Z, r times ionized, with q highly excited electrons. Equations (50 a) and (50 b) are derived respectively from lower and upper limits of the catching power. A closer approximation than either to the catching power can probably be obtained as follows. Consider the normal ion with $z-r-q$ electrons in normal orbits and let it catch q more electrons in succession into highly excited orbits, assuming at each step that the number of possible orbits so obtained is not altered by later captures. Such a calculation will have the effect of replacing $(r+1)^q$ in (50 a) by $(r+1) \ldots (r+q)$, and we obtain the approximation :

$$u_r^z(\mathrm{T}) = \varpi_r^z + \sum_{q=1}^{q=z-r} \varpi_{r+q}^z (r+1)^3 \ldots (r+q)^3\mathrm{B}^q \times \left\{ \frac{\mathrm{V}}{\Sigma_{r,z,q}(r+1)^{\frac{3}{q}} \ldots (r+q)^{\frac{3}{q}}(\mathrm{M}_r^z)_q} \right\}^{\frac{1}{2}q} e^{-\{\chi_r^z+\ldots+\chi_{r+q-1}^z\}/k\mathrm{T}}. \quad (50\,c)$$

In this approximation, which may be preferred to (50 a) or (50 b) in applications, we assert that an $(\mathrm{M}_r^z)_q$ has caught electrons and possesses such a number of possible orbits within its radius of action as if it were a point charge $(r+1)^{\frac{1}{q}} \ldots (r+q)^{\frac{1}{q}}\epsilon$.

These $u_r^z(\mathrm{T})$ of Planck's theory may be used for a direct construction of the characteristic function Ψ of the assembly.

If F_r^z and G are given by equations (5) with the values of this section for $u_r^z(T)$, then

$$\Psi/k = N\left(\log\frac{VG}{N}+1\right)+\Sigma_{r,z} M_r^z\left(\log\frac{VF_r^z}{M_r^z}+1\right), \quad . \quad (51)$$

to which radiation and electrostatic terms may be added as in equation (8). There are in this theory as here developed no excluded volumes.

In applications the most important combination is $u_{r+1}^z(T)/u_r^z(T)$. It will be found that in general one term of (50) is dominant for given density and temperature, and that the dominant terms of $u_{r+1}^z(T)$ and $u_r^z(T)$ generally correspond to equal numbers of electrons in normal orbits, and the loss of one excited electron by the M_{r+1}^z. In this case

$$\frac{u_{r+1}^z(T)}{u_r^z(T)} = \frac{e^{\chi_r^z/kT}}{(r+1)^3 B}\left\{\frac{V}{\Sigma_{r,z,q}(r+1)^{\frac{3}{q}}\ldots(r+q)^{\frac{3}{q}}(M_r^z)_q}\right\}^{-\frac{1}{2}}. \quad . \quad . \quad . \quad (52)$$

If s is the average number of free electrons per atom, then

$$\Sigma_{r,z}\, rM_r^z = s\Sigma_{r,z}\, M_r^z = N.$$

It will then be permissible as a first very rough approximation to write

$$\Sigma_{r,z,q}(r+1)^{\frac{3}{q}}\ldots(r+q)^{\frac{3}{q}}(M_r^z)_q = (s+1)^3\,\Sigma_{r,z}\, M_r^z = (s+1)^2 N,$$

and so

$$\frac{u_{r+1}^z(T)}{u_r^z(T)} = \frac{(s+1)\, e^{\chi_r^z/kT}}{(r+1)^3 B(V/N)^{\frac{1}{2}}}. \quad . \quad . \quad . \quad . \quad (53)$$

Other combinations can be derived from the $u_r^z(T)$ as in § 8.

§ 10. *Comparisons of the foregoing theories.*—A comparison of the foregoing theories can be simply made for the case of a single excited electron. We then have the following results, in which the permanent constants have been given numerical values.

Theory of Urey and Fermi :

$$u_r^z(\mathrm{T}) = \varpi_r^z + 3{\cdot}70 \times 10^{11} \varpi_{r+1}^z (r+1)^{\frac{3}{2}} (\mathrm{V/N})^{\frac{1}{2}} e^{-\chi_r^z/k\mathrm{T}}. \quad (54\,a)$$

Theory of Planck :

$$u_r^z(\mathrm{T}) = \varpi_r^z + 5{\cdot}09 \times 10^{11} \varpi_{r+1}^z \frac{(r+1)^3}{s+1} \left(\frac{\mathrm{V}}{\mathrm{N}}\right)^{\frac{1}{2}} e^{-\chi_r^z/k\mathrm{T}} \quad . \ . \quad (54\,b)$$

Variant of § 7 :

$$u_r^z(\mathrm{T}) = \varpi_r^z + 1{\cdot}45 \times 10^{10} \varpi_{r+1}^z (r+1)^2 \mathrm{T} \left(\frac{\mathrm{V}}{\mathrm{N}}\right)^{\frac{2}{3}} e^{-\chi_r^z/k\mathrm{T}}. \quad (54\,c)$$

In stellar applications T varies from 10^6 to 5.10^7 and $(\mathrm{N/V})^{\frac{1}{6}}$ from perhaps 10^3 to 10^4. There is therefore an extra numerical factor of average value 2000 or so to be inserted in the last formula for a direct comparison in such cases. The numerical factor in the last formula is therefore greater by a factor of rather more than 50 than those of the first two, which may be said to agree. Since, however, the only important function of the u's in applications is u_{r+1}^z/u_r^z the absolute value of the coefficients will only matter in determining the temperature at which the relative importance of the two terms in u_r^z reverses. It is easy to see that the use of any one of these formulæ would lead to almost indistinguishable astrophysical results *. Choice of theory is of minor importance if there is to be only one excited electron.

It appears, however, that the absolute value of the constant at once becomes of major importance when there may be any number of excited electrons and choice of the truest theory imperative. It is impossible to believe that there must be only one excited electron. The more general calculation of the u's here contemplated will have to be used, and it must be presumed that Planck's theory, as given here, is probably the best yet formulated.

The difference of form, however, between (54 *b*) and (54 *c*) suggest that some further modification of Planck's theory may be desirable before extensive astrophysical calculations are undertaken. The T-factor in (54 *c*) arises from the relative velocity of the interacting systems—the greater

* *Cf.* the calculations of Guggenheim, *loc. cit.*

the relative velocity the less the target area, after a certain minimum is exceeded. Such an effect must really be present. The absence of such a factor from Planck's formula is due to this calculation being based on point nuclei *at rest*, unmodified when they are allowed to move. If, however, the nuclei are in relative motion, then it will not necessarily be the nearest which limits the catching region of the nucleus under consideration. Relative to this nearest the energy of the electron need not even be negative. At temperatures sufficiently high the relative motion of the nuclei must become important in increasing the sizes of catching regions. The effect awaits exact investigation. If this is possible in any simple manner, Planck's theory so modified would appear to provide a satisfactory approximation to the true partition functions for atomic ions.

LXXVI. *On the Choice of Striking Point in the Pianoforte String.*

By R. N. Ghosh, *M.Sc., Lecturer in Physics, Allahabad University* *.

[Plate XIII.]

IN a series of papers † it has been shown that the elasticity of the hammer-felt must be taken into consideration to calculate the duration of impact. It is this quantity which controls the quality of the note. The amplitude of partials, their duration, etc., depend upon this. The variation of the tone quality also depends upon the power of changing the duration of impact by "touch." In this paper a preliminary account is given of the experimental investigation on the amplitudes of the partials from a steel string struck at different points, and a comparison has also been made with the theory as given in Phil. Mag. vol. xlix. p. 121 (1925), the result of which is to indicate that the choice of the striking point should be such as to make the ratio of the free period of vibration of the string to the duration of impact equal to 2. Very recently some work has been done in this

* Communicated by Prof. Megh Nad Saha.

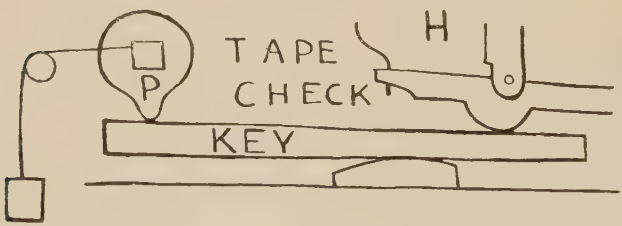
† Phil. Mag. vol. xlvii. p. 1142 (1924); vol. xlix. p. 121 (1925). Proc. Ind. Assoc. Calcutta, vol. x. pt. 1.

direction by others*, but little attention has been paid to the correlation of the results with the theory.

Experimental Methods.

A piano string was fixed over two bridges on a sonometer and kept vertical by suitable supports. The string was struck by a pianoforte hammer and key which were taken out from an actual pianoforte. The system used was a tape check action. The variation of the striking point was made by raising or lowering the sonometer. It was always carefully arranged that the hammer had full play, for if the hammer was very close to the string the note was dull. The point struck was photographed by a falling plate; in some cases the trace of an electrically maintained tuning-fork was simultaneously photographed to obtain the duration of contact. In order to strike the key always with the same force, or to give the hammer the same velocity, a very simple arrangement was made, shown diagrammatically in fig. 1.

Fig. 1.



To a wooden axle a wheel p of the shape shown was fixed just over the key; it was arranged that a kilogram load should always fall through a height of 10 cm. and give one revolution to the wheel, which presses the key instantaneously, thus giving the hammer always the same velocity. The frequency of vibration of the string was found out from the plates in which the simultaneous record of the tuning-fork was obtained. Having no mechanical analyser, the curves were analysed by the schedule method given by H. O. Taylor (Phys. Review, Oct. 1915). For this purpose the curves were magnified 50 times and a faithful trace was taken, then the ordinates were carefully measured. Below is given a table of the amplitudes of five components with different hammers at different points. For the sake of comparison the duration of contact is also given there.

* Phil. Mag. vol. l. p. 491 (1925). Proc. Ind. Assoc. vol. viii. pt. 2.

TABLE I.

Length of the string 100 cm. Freq. 88 per second.
Mass per unit length ·0961 gm. per cm.
Velocity of impact 2×10 cm. per sec.

No.	α.	$\frac{T}{\phi}$.	Hammer No.	1.	2.	3.	4.	5.	Remarks.
1	8	2·3	1	1·33	1·09	·078	·122	·21	
2	11	1·85	1	3·16	2·75	·96	1·06	·031	Fund. max.
3	12·5	1·80	1	2·9	2·6	·90	·91	·24	
4	14	1·56	1	1·8	1·3	·78	·71	·25	
5	16·5	1·44	1	3·07	1·7	·62	·31	·20	
6	20·5	1·1	1	3·66	1·34	·50	·27	·09	Fund. max.
7	12	1·08	3	2·08	1·05	·78	·297	·08	
8	15·2	·97	3	3·4	1·2	·71	·144	·37	
9	17	·91	3	5·09	1·82	·84	·13	0	
10	20	·83	3	5·74	1·08	1·36	·31	0	
11	11·3	2·9	5	·404	1·12	1·15	·25	·13	
12	15·7	2·4	5	1·98	1·48	·47	·29	·30	
13	19	2·1	5	3·29	2·06	·72	·17	·086	Fund. max.

α = Striking distance from nearer bridge.

$\frac{T}{\phi}$ = Free period of vibration of string / duration of impact.

Effective mass of hammer No. 1 = 7·1 gm. $\frac{T}{\mu}=1·3.$

„ „ „ No. 3 = 19·0 gm. $\frac{T}{\mu}=·56.$

„ „ „ No. 5 = 2·6 gm. $\frac{T}{\mu}=0.$

Discussion of Results.

The simple formula for the amplitude of any component has been given in Phys. Review, vol. xxiv. p. 456 (1924). For the same string and the same velocity of impact, the amplitude of the sth component at the point struck is given by

$$A_s = -\frac{\sin^2 s\pi\alpha/l \,.\, \cos\,(s\pi\phi/T)^*}{s(s^2-\frac{1}{4}T^2/\phi^2)}, \quad . \quad . \quad . \quad . \quad (1)$$

discarding quantities which are small.

* Recently the author has been able to make further approximations in the formula.

TABLE II.—$l=100$. Freq. 124. $\rho=\cdot0211$. Velocities of impact arbitrary.

No.	a.	$\frac{T}{\phi}$.	1.	2.	3.	4.	5.	6.	7.	8.	9.	Hammer No.
1	$\frac{1}{6}$	......	1	·24	·111	·072	·047	·03	·033	·37	·36	5
2	$\frac{1}{7}$	......	1	·23	·12	·022	·048	·02	·015	·13	·02	5
3	$\frac{1}{8}$	......	1	·51	·29	·091	·094	·07	·016	·018	·03	5
4	$\frac{1}{9}$	......	1	·34	·098	·095	·041	·106	·032	·034	·01	5
5	$\frac{1}{6}$	......	1	·18	·24	·048	·014	·037	·038	·007	·02	1
6	$\frac{1}{7}$	......	1	·01	·18	·068	·042	·043	·01	·008	·003	1
7	$\frac{1}{8}$	......	1	·09	·012	·04	·007	·023	·02	·018	·18	1
8	$\frac{1}{9}$	......	1	·15	·092	·11	059	·042	·19	·015	·009	1

TABLE III.—$l=100$. Freq. 84. $\rho=\cdot0795$.

No.	a.	$\frac{T}{\phi}$.	1.	2.	3.	4.	5.	6.	7.	8.	9.	Hammer No.
1	$\frac{1}{6}$	1·55	1	·41	·185	·103	·08	·018	·01	·032	·049	1
2	$\frac{1}{7}$	1·67	1	·31	·164	·10	·05	·20	·013	·023	·06	1
3	$\frac{1}{8}$	1·86	1	·69	·083	·17	·12	·04	·017	·017	·041	1
4	$\frac{1}{9}$	1·97	1	1·03	·285	·19	05	·162	·054	·033	·13	1
5	$\frac{1}{6}$	2·48	1	·98	·32	·103	·114	·074	·062	·069	·042	5
6	$\frac{1}{7}$	2·74	1	·75	·66	·25	·25	·031	·08	·023	·07	5
7	$\frac{1}{8}$	2·95	1	1·8	1·2	·63	·05	·11	·146	·035	·06	5
8	$\frac{1}{9}$	3·1	1	1·84	1·03	·53	·54	·28	·095	·054	·09	5

$\frac{T}{\mu}=\cdot11$ for H_1.

Below is given a table of the amplitudes of the fundamental and the octave for different values of $\frac{T}{\phi}$ for the same value of α calculated from (1).

TABLE IV.

No.	$\frac{T}{\phi}$.	1.	2.	3.	Remarks.
1	·5	1·06	·125	......	Fundamental max.
2	·7	·3	·12	......	
3	1·0	1·33	·133	·04	Fundamental max.
4	1·5	·43	·08	......	
5	1·7	1·0	·13	......	
6	2	1	·17	......	Fundamental max.
7	2·5	·55	·20	......	
8	3	·4	·14	·049	

From Table I. we find that the fundamental is maximum at $\frac{T}{\phi}=1$, and $\frac{T}{\phi}=2$, which are theoretically required when

$$\sin^2\frac{s\pi\alpha}{l}$$

remains the same. In the experiments that have been tabulated the ratio $\frac{T}{\phi}$ was changed, firstly by changing the striking distance and secondly by changing the hammer.

$$\frac{T}{\phi}=\frac{1}{\pi N}\left(\frac{T}{M}\right)^{\frac{1}{2}}\left\{\frac{1}{\alpha(1+T/\mu\alpha)}-\frac{1}{4}\frac{\rho}{M}\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad (2)$$

$$M=M_0+\frac{\rho\alpha}{3}=\text{effective mass of hammer.}$$

$$N=\text{frequency, } T=\text{tension.}$$

A correct comparison of Table IV. with Tables I., II., and III. can only be made when the amplitudes tabulated there are divided by $\sin^2\frac{s\pi\alpha}{l}$,

$$A_s=\frac{A_s\,\text{obs.}}{\sin^2 s\pi\alpha/l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The presence of the factor $\sin^2\frac{s\pi\alpha}{l}$ is to increase the

amplitude as we move away from the bridge. If the variation of the amplitude due to change of $\frac{T}{\phi}$ with change of α is much larger than the increase of $\sin^2 \frac{s\pi\alpha}{l}$, the rise and fall of amplitude will still be found. And this is the case in hammers No. 1 and 5, while in the case of hammer No. 3 the amplitudes go on increasing with increase of α. This, as just now pointed out, is due to the fact that the percentage variation of the amplitude due to change in $\frac{T}{\phi}$ is smaller than that of the increase due to $\sin^2 \frac{s\pi\alpha}{l}$. In other words, the effect is masked. At 20 cm. from the bridge in the case of H. 5, $\frac{T}{\phi}=2{\cdot}1$, while in the case of H. 1, $\frac{T}{\phi}=1{\cdot}1$; so that $\sin^2 \frac{s\pi\alpha}{l}$ remains the same in both the cases and the amplitudes of the fundamental, the octave, and the second harmonic are related as

Table V.

3 : 1 : 5/30 for H. 1.

3 : 2 : 7/30 for H. 5.

Hence we find that, though the maximum of the fundamental is almost the same in the case when $\frac{T}{\phi}=1$, or when $\frac{T}{\phi}=2$, the octave and the third components increase in amplitude when $\frac{T}{\phi}=2$. Lastly, reducing the amplitudes to the same scale we obtain

Table VI.

	H. 1.	H. 3.	
1	11	14	$\frac{T}{\phi}=1$.
2	4	7·5	
3	1·4	5·0	

According to the simple theory calculated in Table IV. the amplitudes should be equal, but there are other factors, namely, the stiffness of the string, the reflexions which

influence the amplitudes to a large extent and which we have not taken into consideration. From Table IV. we also find that the amplitude of the fundamental is again maximum when $\frac{T}{\phi}=\frac{1}{2}$. This was not experimentally verified, but the ratio $\frac{T}{\phi}=\frac{1}{2}$ does not seem to be of practical use, for then the reflexions from the farther end in presence of the hammer on the string would render the partials non-harmonic. Discarding this case, we must have the ratio $\frac{T}{\phi}=1$ or 2 to have a large fundamental.

Choice of the Striking Point.—From Table V. we find that the amplitude of the octave and the third component in the case $\frac{T}{\phi}=2$ is greater than in the case $\frac{T}{\phi}=1$. The presence of the third component is theoretically explained by the second term in equation 16 (Phil. Mag. vol. xlix. p. 128, 1925). Further, in this case the impact ceases before the wave reaches the other end. From these considerations it seems, therefore, that the choice of the striking point is made by making the ratio $\frac{T}{\phi}=2$. This had been verified in the case of the piano which I possess. The ratio $\frac{T}{\phi}$ was calculated from formula (2).

$l=91{\cdot}5$ cm. $\rho={\cdot}137$ grm. per cm.

Tension $=4{\cdot}57\times 10^7$.

Freq. 100 approx.

Maxima at 11·1 cm. (experimentally found).

Mass of hammer 10·5 gm.

$\frac{T}{\phi}=1{\cdot}87$. [From (2).]

Hence we see that the choice of the striking point depends upon the ratio $\frac{T}{\phi}$ which must be 2 : 1.

This ratio can be achieved in practice in two ways, viz., by changing the mass of the hammer or the striking distance so that their product remains constant. Now α the striking distance should not be greater than a finite value, otherwise the waves undergo modifications from reflexions from the farther end and the components would be rendered

non-harmonic for reasons mentioned before. Also α should not be very small, for on account of the factor $\sin\frac{s\pi\alpha}{l}$ the amplitude of the resulting vibrations would be very small. Hence α must lie somewhere between 1/9 to 1/7 l. When α is fixed the mass of the hammer is determinate. For the best musical note the partials must converge in a particular way. For a given value of $\frac{T}{\phi}$ the convergence of the partials is the same when $\sin\frac{s\pi\alpha}{l}$ is constant. But on account of the latter factor the convergence is different at different points, even if $\frac{T}{\phi}$ is made the same at different points of the string by arranging so that the product of the mass of the hammer and the striking distance remains the same. The value of α for the best musical effect, therefore, also depends upon the factor $\sin\frac{s\pi\alpha}{l}$. This point is under investigation with the help of a piano tuner.

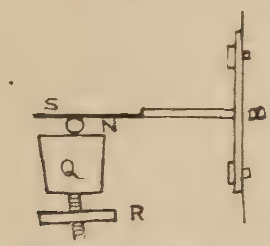
Coming back to the comparison of Tables III. and IV., we find that the ratio of the amplitudes of the fundamental and the octave is the same for a given value of $\frac{T}{\phi}$ as indicated in Table IV., *e.g.* when $\frac{T}{\phi}=1{\cdot}55$ the theoretical value of the ratio is ·44, and experimentally it is found to be ·41. Again, when $\frac{T}{\phi}=2$, the ratio is 1·17 and experimentally it is 1·03; when $\frac{T}{\phi}=1{\cdot}7$, the ratios are ·6 and ·3. Similarly the theoretical conclusions for other values of $\frac{T}{\phi}$ are approximately verified experimentally.

Sound Board.

The effect of varying the striking point on the string on the amplitude of vibration on the sound-board was also investigated. For this purpose a piano whose front part was taken away was used. The velocity of impact was kept constant by the key and wheel arrangement described before. For photographing the vibrations of the sound-board, a steel strip S was soldered to a thick piece B perpendicularly and the piece was screwed to the sound-board. The strip pressed against a rolling needle N supported on a screw top which could be raised or lowered at pleasure;

this was firmly kept in position by another nut R. To the rolling needle a small concave mirror was attached, and a spot of light from an arc lamp was focussed on the moving photographic plate. Pl. XIII. figs. 3, 4, 5, 6, &c. show the vibration curves at different striking points for the same velocity of impact. One very striking phenomenon is the rise and fall of the amplitude of vibration. In some cases the amplitudes

Fig. 2.



swell out first and then diminish steadily. At other points the amplitude passes through small rise and fall and then attains the maximum value, after which there is a steady fall. When the striking distance is small the rise and fall do not appear to be marked, but at greater distances the number of rise and fall and the variation are very marked, as can be observed from the pictures (the photographic plate was dragged at approximately the same velocity). A fuller account with the theory of the vibrations of sound-board will be presented shortly.

Measurements were taken of the biggest amplitude at different points and the average values are tabulated below:—

No,	$\frac{a}{l}$.	Amplitude.	Reduced amplitude.
1	$\frac{1}{10}$	1·4	4·5
2	$\frac{1}{8 \cdot 3}$	1·75	4·9
3	$\frac{1}{7 \cdot 3}$	1·4	3·4
4	$\frac{1}{6 \cdot 3}$	1·9	3·8
5	$\frac{1}{5 \cdot 5}$	1·4	2·6
6	$\frac{1}{5 \cdot 3}$	2·0	3·6
7	$\frac{1}{4 \cdot 6}$	2·4	3·8
8	$\frac{1}{4}$	2·8	3·8

The amplitudes at different points undergo a variation on account of the change in the value of $\sin\frac{s\pi\alpha}{l}$, and hence they must be reduced to the same scale by dividing them with $\sin\frac{s\pi\alpha}{l}$; column 3 was obtained in this way, and we find that the amplitude is maximum at $\frac{\alpha}{l}=\frac{1}{8\cdot 3}$.

The vibration that results in the sound-board is a forced vibration, and it is expected that the maximum forced vibration would result when the force is maximum. Now we have seen that at $\alpha=11\cdot 1$ the ratio $\frac{T}{\phi}$ for the same piano string and hammer system is 2. Hence the effect observed is simply due to the maximum force on the bridge due to the maximum vibration of the string. The sound-board shown by Berry * has a minimum free vibration at this place.

Conclusion.

The experimental results of analysis of different vibration curves obtained by striking the string at different points with the same velocity are :—

(1) Fundamental is maximum when $\frac{T}{\phi}=1$.

(2) Fundamental is maximum when $\frac{T}{\phi}=2$.

(3) The first and second harmonics are stronger in case 2 than in 1.

(4) Choice of the striking point in the piano is made in such a way so as to obtain $\frac{T}{\phi}=2$.

(5) The sound-board reproduces the maximum vibration of the string at $\frac{T}{\phi}=2$.

(6) The choice of the striking point should be such that it lies between 1/9 to 1/7 of the length of the string.

* Phil. Mag. xix. p. 647 (1910).

The author begs to record his debt of gratitude to Prof. M. N. Saha for his kindly supplying him with a pianoforte.

Physics Department,
Allahabad University.
September 17, 1925.

Note added in proof.

Further extensions of Table (I.) :—

$l=95$ cm. Freq. 130, $\rho=\cdot022$ grm. per cm.

$T=1\cdot34\times10^7$. $\alpha=11$ cm. Const.

No.	$\frac{T}{\phi}$	1.	2.	3.	Remarks.
1	1·3	4·7	1·2	1·1	
2	·98	4·8	1·1	·32	
3	·52	1·27	1·48	·69	Different hammers.
4	·82	4·3	·69	·56	
5	1·1	4·9	1·0	·40	

$l=92$ cm. $T=1\cdot88\times10^7$. Freq.$=160$.

$\frac{T}{\mu}=0$. $M=2\cdot6$ grm. Const.

No.	a.	$\frac{T}{\phi}$	Reduced amplitude. 1	2	3
1	6	1·9	23·5	6·2	·42
2	8	1·62	23·3	4·0	·93
3	11	1·36	18·1	1·4	·46
4	16	1·1	20·2	·6	·38
5	18·5	·95	15·0	1·1	1·07

LXXVII. *The Refractive Index of Gases and Vapours in a Magnetic Field.* By RONALD FRASER, *B.Sc., Assistant in Natural Philosophy at the University of Aberdeen*.*

Introduction.

THE experiments of Gerlach and Stern † have shown that certain atoms are orientated in a magnetic field in accordance with the theory of space quantization developed by Sommerfeld. On the other hand, Glaser's results on

* Communicated by Prof. G. P. Thomson, M.A.

† Gerlach and Stern, *Ann. Phys.* lxxiv. p. 673 (1924); Gerlach, *ibid.* lxxvi. p. 163 (1925).

the variation of the susceptibility of the diamagnetic gases H_2, N_2, and CO_2 with change of pressure *, point, though with considerably less certainty, to the orientation of molecules in the field.

It seemed reasonable to suppose that certain optical effects might follow from the presence of such orientation. Suppose, for example, that light is passed through a gas composed of single-quantum atoms all orientated in the direction of a uniform magnetic field, the path of the beam being parallel to the direction of the field ; then the electric vector will lie always in the invariable plane of the atoms. When, however, the same atoms are orientated at random, that is, when no field is present, the direction of the electric vector can bear no particular relation to the orbital planes. It seems reasonable to suppose that the polarization of the atoms induced by the light is not the same in the two cases ; and hence a difference in *refractive index* of the gas with and without the presence of the magnetic field might conceivably be expected.

The experiments to be described were undertaken with a view to detecting such an effect.

Experimental Arrangements.

The apparatus employed was a Jamin interferometer, one tube of which contained the substance under examination, the other being evacuated. The tubes were surrounded for their whole length by an air core solenoid. A shift of the interference fringes on throwing on the field was looked for.

The wave-length employed was uniformly the mercury green. Light from a quartz mercury arc, suitably filtered, was focussed on the slit of a collimator, the lens of which was furnished with a diaphragm 1·5 cm. in diameter. The collimated beam then fell on the first of the Jamin mirrors, which were supplied by Hilger. The tubes, being intended for the examination of sodium, were of steel : being 100 cm. long, 1·5 cm. in diameter, and closed with worked glass disks supplied by Hilger. Iron or steel was rigidly excluded from the rest of the apparatus. The interference fringes were viewed in a telescope furnished with an ocular micrometer. The breadth of the fringes was 3 scale divisions ; further broadening caused the edges to become unduly blurred. A movement of a thirtieth of a fringe could readily be detected.

* Glaser, *Ann. Phys.* lxxv. p. 459 (1924).

It was essential to have the fringes exceedingly steady, so that a given line of the ocular scale could be brought on to the edge of one of the fringes and held there until the field was thrown on. Special precautions were taken therefore to eliminate vibration. The apparatus was supported on a heavy slate slab which rested on a concrete pier built solid with the concrete floor in the basement of the building. The Jamin mirrors and the tubes were supported on heavy brass castings, the bases of which were hand-scraped flat to a surface-plate before being bolted down on the slate. All work was done at night and trouble from vibration was entirely absent.

With a current of 25 amps. in the solenoid, the field inside the steel tubes, as measured with search-coil and fluxmeter, was 184 gauss. The tubes were carefully demagnetized before each observation.

Experiments with H_2, O_2, N_2, CO_2.

It is essential that the pressures under which the gases are examined should not be too high, it being necessary that the period of the Larmor precession should be at least of the same order as the mean time between collisions. Otherwise it appears that, in accordance with the periodicity condition, space quantization is not sharply defined. With the fields employed, pressures higher than 1 cm. are to be avoided.

In examining the above gases, both tubes were evacuated to ·001 mm., and the gas to be examined admitted to one of them up to a pressure of ·6 to ·8 cm. The entrance of the gases caused a shift of some six to eight fringes with the apparatus used, so that reading to a thirtieth of a fringe, a change of half a per cent. in the refractive index, due to the magnetic field, would have been observable.

Preliminary experiments were made with dry air, and a null result obtained.

H_2 and O_2, prepared by the electrolysis of carbonate free sodium hydroxide ; N_2 from the air, oxygen being absorbed by alkaline pyrogallol, CO_2 by potassium hydroxide ; CO_2 from pure marble and hydrochloric acid, were examined. The gases were dried over phosphorus pentoxide before being admitted to the apparatus. Three independent observations were made on each gas. In each case, the effect of introducing a nicol in the path of the illuminating beam was tested. The prism was orientated to give plane polarized light with the electric vector vertical ; the gases were contained in the tube receiving light from the *face* of the first

Jamin mirror, to avoid the ellipticity introduced by reflexion from the silvered back of the mirror.

Uniformly null results were obtained *.

Sodium.

It might be, as Pauli has pointed out in a discussion of Glaser's results †, that the number of possible orientations for the molecules of the gases examined is so great that no distinction can safely be drawn between quantum and classical diffuse orientation. Such a possibility is excluded in the case of sodium, which, as an alkali metal, may reasonably be supposed to possess a single quantum atom, orientating with its axis in the direction of a uniform field. The conditions for observing any possible alteration in the refractive index are therefore favourable for sodium.

For the experiments with sodium the ends of the tubes were cooled by means of water-jackets, and both were heated between the water-jackets by an electric furnace. The open ends of the solenoid were packed around the water-jackets with cotton-wool, and the furnace lagged with asbestos. Mirage was very slight.

The sodium, freed from naphtha by distillation, was introduced into one of the tubes, which was immediately evacuated and heated to a temperature of 500° C. It was maintained at this temperature for five or six hours, the pump being in operation throughout. Pumping was continued until the McLeod gauge showed less than ·01 mm. Observations were taken in a temperature range of 475°–410° C., the apparatus being continuously evacuated during the experiments.

Vapour pressures of the alkali metals are difficult to measure, and the agreement between independent observations leaves much to be desired. Accepting the recent determinations of Rodebush and de Vries ‡, interpolation gives a pressure range of 2·5–0·5 mm. for sodium vapour

* The present experiments on H_2, O_2, N_2, and CO_2 confirm similar observations on H_2, O_2, and He, made in the Cavendish Laboratory by Mr. H. W. B. Skinner, who has very kindly communicated his results to me. Skinner, using a sodium flame as source, finds that a transverse magnetic field of some 10,000 gauss has no effect on the refractive index for pressures varying from 0–760 mm. He has also established the absence of double refraction independent of the field strength for H_2, O_2, and He, within the same pressure range.

† *Phys. Zeit.* xxvi. p. 212 (1925).

‡ Rodebush and de Vries, Journ. Amer. Chem. Soc. xlvii. p. 2488 (1925).

between 475° and 410° C. On heating to 475° six fringes moved across the reference line of the ocular. The furnace was switched off, and observations were taken as successive fringes returned to the reference line as the vapour cooled. Two experiments were made with sodium, in each case with illumination by ordinary and plane polarized light. Null results were obtained *.

Discussion.

The absence of any observable change in the refractive index when the field was thrown on indicates that within the limits of observation the atoms and molecules examined react to light in a manner independent of their orientation—in short, that they behave as if they were optically isotropic.

Isotropic behaviour of this kind is of considerable theoretical interest, presenting as it does in a slightly different aspect an anomaly in the theory of space quantization which seems to need further investigation. Stern † first pointed out that anisotropy, resulting in a magnetic double refraction independent of the field strength, appeared to follow as a necessary consequence of the theory ‡. Its absence in sodium vapour was demonstrated by Gerlach and Schütz §, for the immediate neighbourhood of the D lines; while the present observation on sodium is for a region well removed from the D lines. After the experiments described here were in progress, Heisenberg ‖ pointed out that the absence of double refraction independent of the field strength is connected formally with the assumed absence of total polarization in a Zeeman multiplet; a beginning towards accurate intensity measurements of Zeeman components is, however, only now being made, chiefly by Ornstein and his co-workers in Utrecht. Again, Heisenberg's conclusion strictly applies, apparently, only to those absorption lines which show a normal triplet; nevertheless, it would be of interest to decide whether

* Recent experiments on the breadths of absorption lines of Na vapour (Harrison and Slater, Phys. Rev. xxvi. p. 176, 1925), indicate the presence of diatomic molecules in appreciable numbers above 450°. The recognition of this factor makes the present observation on Na rather less unequivocal than appeared at first.

† Stern, *Zeit. fur Phys.* vii. p. 617 (1922).

‡ Magnetic double refraction, influenced by the field strength, in the neighbourhood of an absorption line (Voigt-Wiechert double refraction) is, of course, well known, and due to well recognized factors.

§ Gerlach and Schütz, *Naturwiss.* xi. p. 637 (1923). See also footnote above.

‖ Heisenberg, *Zeit. f. Phys.* xxxi. p. 617 (1925).

a substance will show anisotropic behaviour in the region where an intermediate stage of the Paschen-Back effect is displayed by one of its absorption lines.

I am glad of this opportunity to express my gratitude to Professor G. P. Thomson for much helpful discussion. I am indebted to Mr. C. G. Fraser, instrument maker in the Department, for invaluable technical assistance.

LXXVIII. *On Entropy of Radiation.* II. *By* MEGHNAD SAHA *and* RAMANI KANTO SUR, *Physics Department, Allahabad University, India* *.

IN a previous paper, it has been shown that the thermodynamical probability of a system is given by the law

$$W=\{\gamma\}/\{\gamma\}_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where $\{\gamma\}$ = phase-space described by the system at temperature T_0, $\{\gamma\}_0$ = phase-space described at absolute zero. It was shown that the absolute value of entropy of perfect gases could be deduced from this theorem.

The same formula can be applied for deducing the entropy of radiation. Since the time when Bartoli deduced the existence of radiation pressure from thermodynamical reasoning, it has been customary to look upon radiation as a sort of perfect gas. But the analogy is often misleading, for the energy of gaseous molecules is capable of continuous variation, while according to Planck, radiant energy or energy of light pulses can vary only in multiples of $h\nu$. If E_ν = total energy of frequency ν, then

$$E_\nu=N_\nu \, . \, h\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

N_ν = number of energy elements.

In calculating the probability, we have further to find out the number of ways in which a quantum can be contained within unit volume. This is equal to $A=\frac{8\pi\nu^2}{c^3}$. The deduction of this theorem forms the greatest difficulty in the theory of black body radiation. In the original method of deduction by Jeans and others, $\frac{8\pi\nu^2}{c^3}$ represents the total number of stationary waves in unit volume having their

* Communicated by the Authors.

frequency between ν and $\nu+1$. It is deduced in a most complicated way from electromagnetic considerations.

Bose has recently given a very elegant and simple method of deducing the theorem

$$A=\frac{8\pi\nu^2}{c^3}, \quad \ldots\ldots\ldots \quad (3)$$

which is reproduced here.

According to modern conceptions, a pulse of light carries with it the momentum $\frac{h\nu}{c}$ in the direction of its motion. It has got the components

$$p_x, p_y, p_z, \text{ where } p_x^2+p_y^2+p_z^2=\frac{h^2\nu^2}{c^2}.$$

The phase-space described by the pulse in its translatory motion is, according to Planck,

$$\ldots\iint dp\,dq\ldots=\ldots\iiint_{\nu}^{\nu+1} dx\,dy\,dz\,dp_x dp_y dp_z=\frac{4\pi h^3\nu^2}{c^3}V. \quad (4)$$

According to the quantum theory, the phase-space can be split up into cells each of volume h^3, hence the total number of cells

$$=\frac{4\pi h^3\nu^2}{c^3}V/h^3=\frac{4\pi\nu^2}{c^3}V, \text{ or } \frac{8\pi\nu^2}{c^3}V \quad \ldots \quad (5)$$

when we take both the polarized pulses. The number $P=\frac{8\pi\nu^2}{c^3}$ represents the total number of ways in which a quantum $h\nu$ can be contained within unit volume. The idea is therefore the same as the number of stationary waves.

The essential point in the above argument is that the *translatory motion* of a pulse of light can be treated according to the quantum theory, viz., $\int dp\,dq=h$ for any one of the degrees of freedom of the pulse of light.

We can now calculate the entropy of radiation by using the relation

$$W=\{\gamma\}/\{\gamma\}_0.$$

Now $$\{\gamma\}=\Pi(\mu)P, \quad \ldots\ldots\ldots \quad (6)$$

where $\{\mu\}$ = phase-space described by one pulse in its internal electromagnetic vibrations, P = permutability of the pulses. We are not yet acquainted with any method for expressing the internal vibrations within a light-pulse in terms of Hamiltonian coordinates. Planck and other authors, *e. g.* Darwin and Fowler, identify the pulse with some

resonator—Hertzian oscillator, or the Bohr-Vibrator. But we think it may be possible, in the case of a free pulse, to avoid this appeal to material carriers. At any rate, we assume that the pulse is subject to Hamilton's equation

$$\iint dp\, dq = h,$$

for each of its degrees of vibrations.

Then $$\Pi(\mu) = h^{3N_\nu},$$

which means that the pulses do not interchange energy, like gas-molecules, but are independent of each other.

$$P = \frac{A+N\,!}{A\,!\;N\,!}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

because any one of the cells may contain $0, 1, 2 \ldots N_\nu$ pulses.

Thus $$\{\gamma\} = h^{3N_\nu} \frac{A+N\,!}{A\,!\;N\,!}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We have now to find out the value of $\{\gamma\}_0$. This brings us to the point: how we can reach the absolute zero by using radiation as the working substance in a Carnot reversible engine as was first done by Bartoli. Wien showed that we can pass from a radiation space at temperature T to a space at temperature T′ by a virtual slow displacement of the walls. The wave-lengths of radiation enclosed within the space are changed according to the relation

$$\lambda T = \lambda' T',$$

or $$\nu = \alpha T.$$

Hence at $T=0$, $\nu=0$, *i. e.* at absolute zero, it is not possible to have any radiation at all.

This brings us to an interesting analogy. We have seen in the previous paper that if we use a gas as a working substance in the Carnot cycle, absolute zero can be attained only when all matter has been annihilated. The present theorem tells us that if we use radiation as a working substance, absolute zero can be attained in a space where all radiation has been completely annihilated.

We thus obtain $A=0, \quad P=1,$

and $$\{\gamma\}_0 = \Pi(\mu) P = h^{3N_\nu}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\therefore \quad W = \{\gamma\}/\{\gamma_0\} = \frac{A+N\,!}{A\,!\;N\,!}, \quad . \quad . \quad . \quad (10)$$

from which the value of S can be easily deduced.

If we use $A_\nu d\nu$, $N_\nu d\nu$ instead of A and N, we obtain

$$\text{Probability } W = \frac{(A d\nu + N d\nu)\,!}{A d\nu\,!\;\; N d\nu\,!}.$$

It is easy to see that this equals

$$\left\{\frac{(A_\nu+N_\nu)\,!}{A_\nu\,!\;N_\nu!}\right\}^{d\nu}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or in other words,

$$Sd\nu = d\nu\,.\,\kappa\log\frac{(A_\nu+N_\nu)\,!}{A_\nu\,!\;N_\nu\,!}, \quad . \quad . \quad . \quad . \quad (12)$$

$S_\nu d\nu$ now denoting entropy of radiation having their frequency between ν and $\nu + d\nu$.

The value of S_ν, U_ν can be calculated with the aid of the above expression, and the relation $\frac{dS_\nu}{dU_\nu}=\frac{1}{T}$, but as these calculations are to be found in every standard text-book on radiation, they are not reproduced here.

LXXIX. *Notices respecting New Books.*

The Surface-History of the Earth. By John Joly, Sc.D., F.R.S., Fellow of Trinity College, Dublin. (Oxford University Press. Royal 8vo. 192 pages, 13 plates, 11 figures, and an Oro-Bathygraphical Chart of the World. 8*s*. 6*d*. net.)

IN this well printed and illustrated book Professor Joly puts forward a theory of the past history of the earth which differs materially from the one generally accepted. As the earth after its ejection from the sun gradually cooled a solid crust was first formed on the surface where gravitational forces had placed the liquid constituents of least density. The contraction which generally accompanies solidification might lead to the sinking of the material first solidified, but eventually a continuous solid crust would be formed which would be supported hydrostatically by the liquid or semi-liquid beneath it. This theory of the hydrostatic support of the solid crust and its consequences is known as Isostasy. The absence of internal tides and the presence of seismic waves lead to the conclusion that the earth is now solid, and as its still hot interior cools and therefore contracts the outer shell has to shrink like the skin of a drying apple and does so, producing at intervals earthquakes and at times geological revolutions. It is on the origin of these revolutions that Professor Joly differs from the above outline. He believes that the radioactive material in the earth's crust is more than sufficient to supply the heat lost from its surface and the surplus heat accumulates in a layer about 70 miles below the surface. The rock in this layer slowly melts, expanding as it does so and exerting pressure on the crust above it. The crust at times gives way producing earthquakes and geological revolutions as under the former theory. The shrinkage theory provides an explanation of the phenomena so long as there is loss of heat by the interior, the bursting theory provides it so long as radioactive material is present in sufficient quantity. There are, however, several difficulties to be overcome before the new theory can be accepted

as satisfactory. One of these is the concentration of the surplus heat from radioactive changes in a particular layer, and another the secular rise of temperature of the earth during the whole of its past history owing to the amount of radioactive material postulated. The author unfortunately bases his calculations of the expansion on melting of the rocks 70 miles below the surface on the 10 per cent. increase of volume found when rocks melt at atmospheric pressure. Since a pressure of 12,000 atmospheres is known to reduce the volume increase of a solid on melting to less than half its value at atmospheric pressure, a serious revision of these calculations is necessary.

While the book cannot be said to establish the theory which it advances, it is thoroughly stimulating and will result in a more careful and complete examination of the problems which the physical history of the earth presents. C. H. LEES.

The Electron. By R. A. MILLIKAN. Second Edition. (University of Chicago Press. Price 9*s.* 6*d.*)

A System of Physical Chemistry. Vol. II. *Thermodynamics.* By W. G. McM. LEWIS. Fourth Edition. (Longmans. Price 15*s.*)

Exercises in Practical Physics. By Sir A. SCHUSTER and C. H. LEES. Fifth Edition. (Cambridge University Press. Price 12*s.* 6*d.*)

THE three books cited above have little in common except that their excellence, each in its particular field, has led to repeated calls for new printings, for, while Professor Millikan's book is ostensibly only in its second edition, it has already gone through eleven impressions. Since it may be assumed that they are already familiar to most readers of the Philosophical Magazine, it is necessary to do little but indicate the changes made in the latest edition as compared with the previous one; and, since in the case of the two latter books these changes are comparatively slight, the books have been placed together.

Professor Millikan's first edition was published in 1917, and on account of the rapid advances in some of the subjects which he handles, there has been a certain amount of completely new matter to incorporate. There is a brief reference to Aston's work on isotopes (not indexed, by the way). Bohr's periodic n_k scheme is described, with the well-known diagrams of atomic structure of typical atoms first published by Kramers. Many other pieces of recent work have been embodied in the last two chapters, which deal respectively with the Structure of the Atom and the Nature of Radiant Energy. Among these may be mention·d C. D. Ellis's work on the nuclear γ rays, the collisions of the second kind of Klein and Rosseland, and the intriguing Compton effect, the last-named being illustrated by a plate reproducing an excellent photograph showing the displaced lines. The work of the author and Bowen on the spectra of multiply ionized atoms is all too briefly noted. All these features of recent research are described with the conciseness and clarity which are so marked a feature of the book as a whole. Professor Millikan needs no recommendation to the readers of this Magazine, and so the reviewer will spare them a eulogy.

Professor W. C. McC. Lewis has added to his book an account of G. N. Lewis's treatment of solutions, as described in G. N. Lewis and Randall's 'Thermodynamics,' and of one or two other recent investigations in chemical thermodynamics.

Sir Arthur Schuster and Professor C. H. Lees have replaced some of their simpler experiments by somewhat more advanced ones. The book, it will be remembered, is designed to cover adequately all the experimental work required for a pass degree, and the standard demanded seems to be advancing. These two books are so well known that no more need be said.

Mémorial des Sciences Mathématiques.

1. *Sur une forme générale des équations de la dynamique.* By PAUL APPELL.
2. *Fonctions entières et fonctions méromorphes.* By G. VALIRON.
3. *Séries hypergéométriques de plusieurs variables, polynomes d'Hermite et autres fonctions sphériques de l'hyperespace.* By PAUL APPELL. (Gauthier-Villars. Price 10 francs each.)

THESE booklets are the first three of a series, to comprise about one hundred small volumes, written by eminent Continental mathematicians, and published under the auspices of many leading mathematical societies. The aim of the series is to deal with theories of modern mathematics so as to appeal to the research student, and also to the professed mathematician who desires an acquaintance with the present position, and possibilities, of branches of the science outside his own range of work. Each volume is to contain a short introduction to its subject, a detailed description of the main theorems already acquired and indications of probable lines of future research, ending with a sufficient bibliography.

Outlines of proofs and methods special to the subject will be included in the scope of most of the volumes, but critical comparison of alternative methods will not be introduced. Such a collection should then occupy a position between the general treatise and the encyclopædia; but the exact position may well be lacking in definiteness unless the general editor be given wide powers, and exercise his functions extensively. Detailed discussion of elementary problems in illustration of general theorems, on the one hand, and, on the other, austere lists of theorems without discussion or interconnecting matter are both possible dangers.

The three volumes under review show that these and, doubtless other dangers have been successfully avoided, and within the limits of fifty to seventy pages are comprised clear and readable accounts of the theories considered. The first volume deals with Appell's own method of forming the equations of dynamics by means of the "energy of accelerations,"

$$\Sigma \tfrac{1}{2} m(\ddot{x}^2 + \ddot{y}^2 + \ddot{z}^2),$$

whilst the contents of the others are sufficiently described by their titles. No very serious misprints have been noticed.

LXXX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 704.]

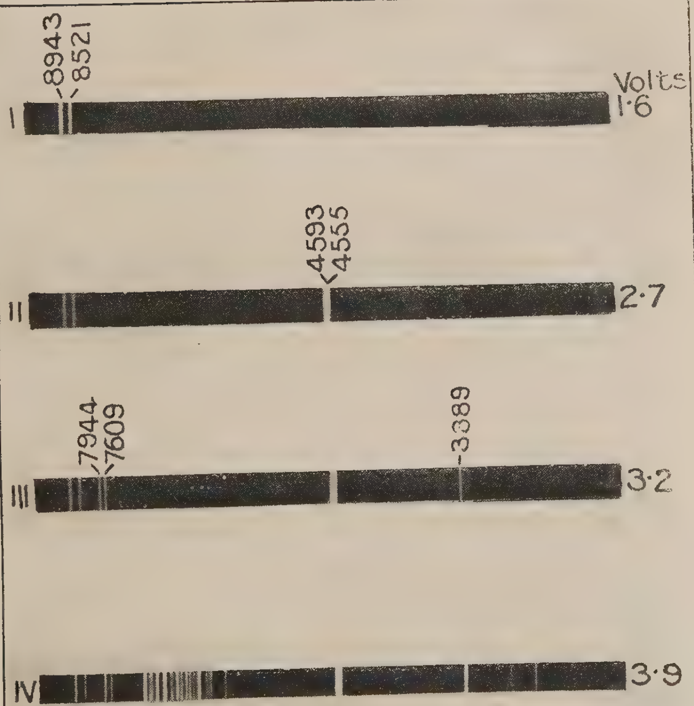
December 2nd, 1925.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

THE following communication was read:—

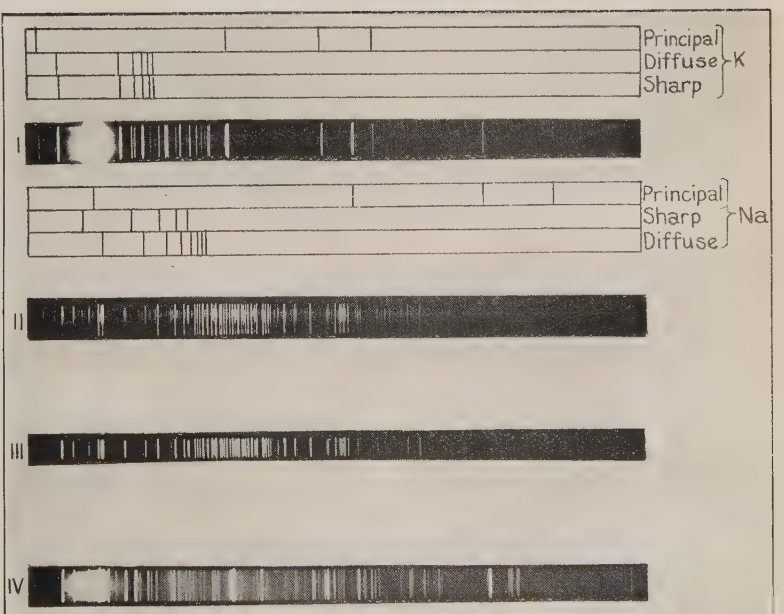
'The Depth of Origin of Earthquakes.' By Richard Dixon Oldham, F.R.S., F.G.S.

Methods of determining the depth of origin of an earthquake, dependent on observations of the time of occurrence, demand records of a degree of precision, and in numbers, which are seldom available. The same objection applies to the Dutton method, based on variation in the intensity of shock; but the method is capable of a simplification which will make it applicable to any case where the area affected by the sensible shock, and the maximum degree of violence attained, can be determined. The original method has been examined, and it is shown that, although the method is sound in principle, two important errors have been introduced in the application. Acceleration has been taken as the measure of intensity, whereas the formula demands that the product of maximum acceleration and amplitude of displacement should be used; and the effect of absorption of energy in transmission has been treated as negligible. It is shown that either of the errors so introduced would be material, but, being opposite in sign and about equal in amount, they nearly neutralize each other, with the result that the depth obtained is approximately correct. The simplified method is applied to the discussion of the Italian record for the years 1897–1910, comprising 5605 distinct shocks, it is found that more than 90 per cent. of these originated at depths of less than 10 km., and mostly round about 5 km.; while only 1 per cent. originated at depths exceeding 30 km. This is in strong contrast with the depths of origin of the distant records, which have been computed by different workers at figures ranging from 50 km., in a few cases, to, in most cases, 100 km. or more. From this it is concluded that the ordinary local earthquake, which can be felt, differs from that which gives rise to distant records, not merely in magnitude, but also in character of cause and origin; in those cases where distant records accompany a destructive earthquake the disturbance has a twofold origin, the episeism, or surface-shock, by which the damage is directly caused, being a secondary result of the bathyseism, which is the origin of the distant record. The great number of local shocks are purely episeisms, without any recognizable bathyseism; in rare instances the sensible shock appears to have originated directly from the bathyseism, unaccompanied by any recognizable episeism.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

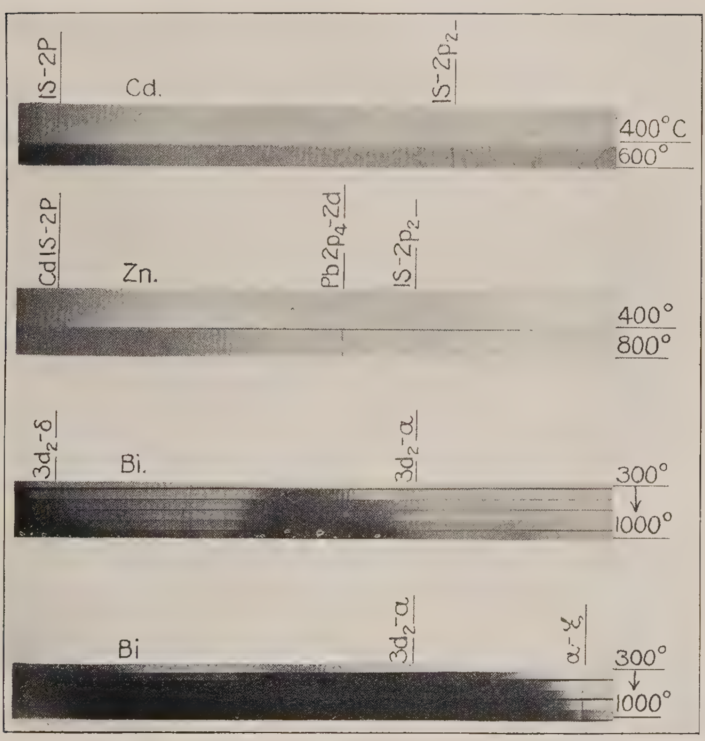


The spectrum of Caesium at low voltages.



The arc and interrupted arc spectra of Sodium and Potassium.

FIG. 2.


1S-2P
Cd.
1S-2p2
400°C
600°
Cd 1S-2P
Zn.
Pb 2p4-2d
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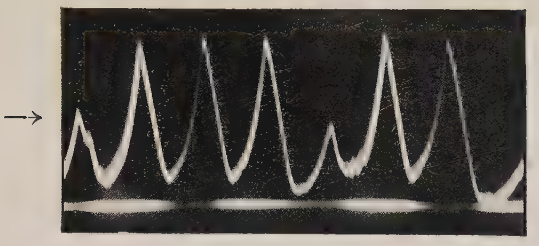

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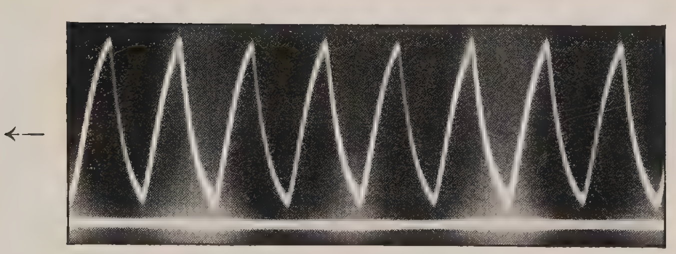

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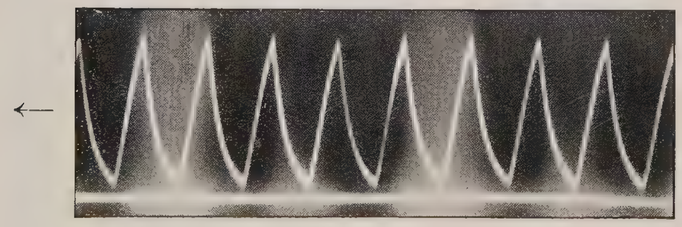

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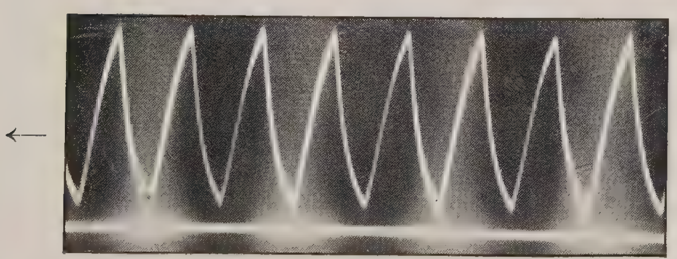
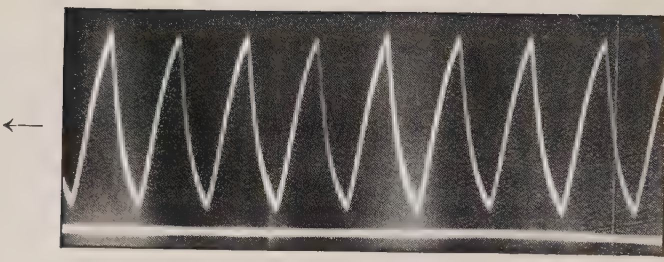


No. IV. *a*.



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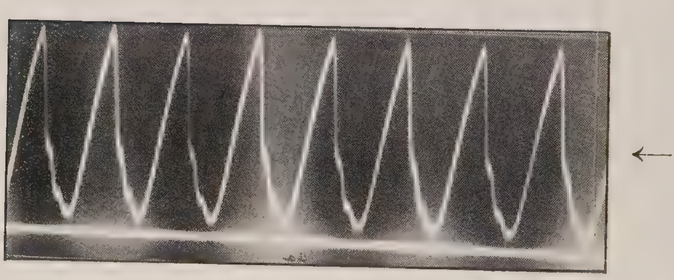

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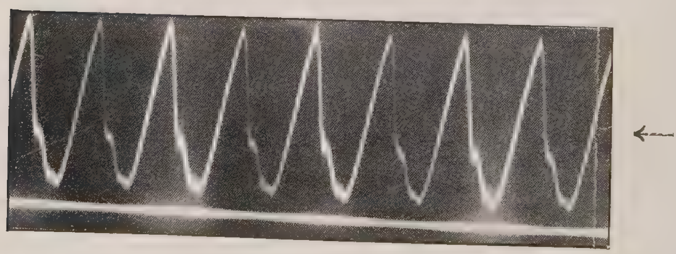
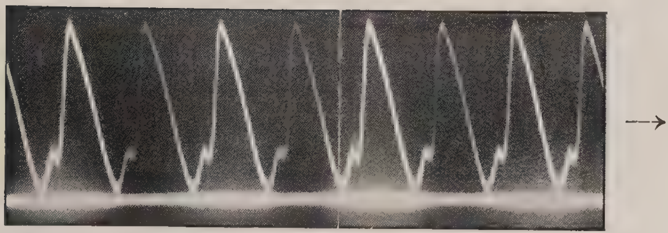
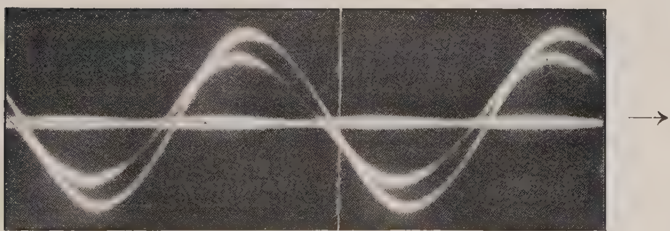


No. V. *b.*

Current Wave Form in an Electrically Maintained Tuning-fork Circuit.



No. V. *c*.



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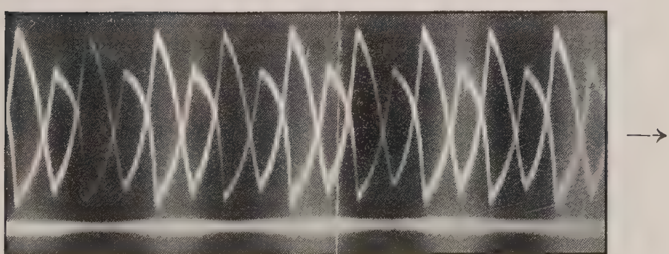

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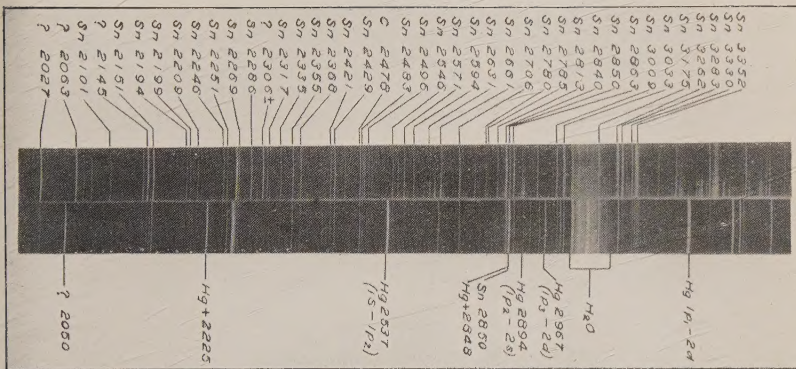


FIG. 2 *a*.

FIG. 2 *b*.

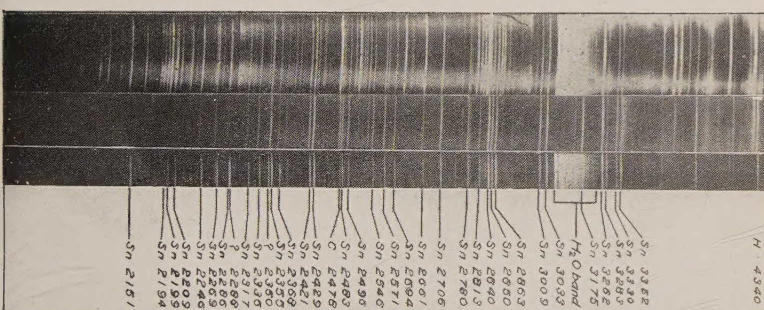


FIG. 3 *a*.

FIG. 3 *b*.

FIG. 3 *c*.

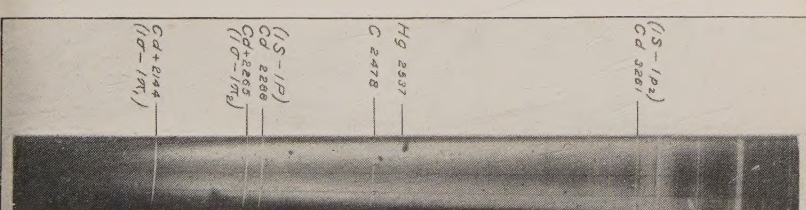


FIG. 4.

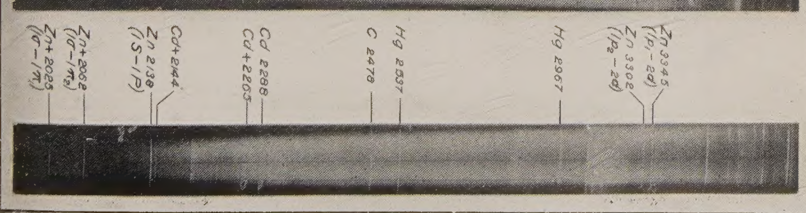
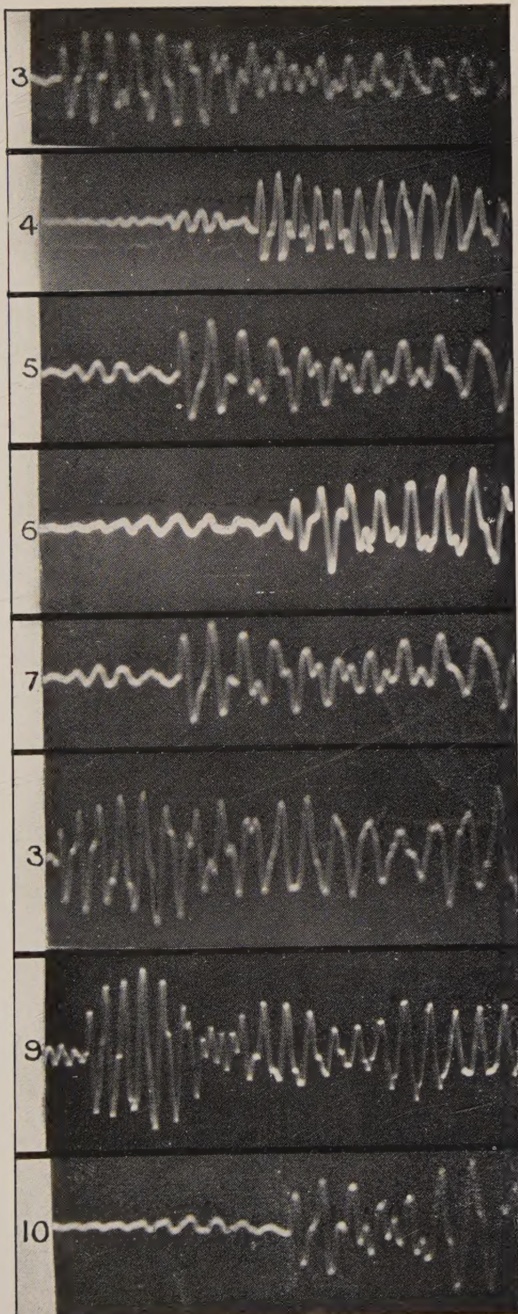


FIG. 5.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